An Analysis of Student Performance on Acid-Base Equilibria Problems Before and After Instruction

Undergraduate Research Thesis

Presented in Partial Fulfillment of the Requirements for Graduation with Honors Research Distinction in Chemistry in the Undergraduate Colleges of The Ohio State University

by

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Abstract

Solving quantitative problems is an important feature of most undergraduate chemistry courses. Students frequently struggle with these complex quantitative problems because they require mathematical skills, conceptual understanding, and problem-solving strategies. The topic of acid-base equilibria includes quantitative problems that are difficult for many students in General Chemistry, and this same topic is also an important part of upper-level Analytical Chemistry courses. General Chemistry students are novices when they first encounter this topic, and students that complete Analytical Chemistry can be considered undergraduate experts. This investigation aimed to understand how novice and expert students solve acid-base equilibria problems and identify their problem-solving strategies, the heuristics they use, and any essential skills that they demonstrate. Two open-response instruments were written to elicit student problem-solving for questions involving strong electrolytes, weak electrolytes, neutralization reactions, and titrations. The study design included testing before and after instruction for General Chemistry students (n=169) and Analytical Chemistry students (n=34), and class experiences characterized for both courses in terms of lecture, homework, and laboratory activities. The open-response data were analyzed using a qualitative approach to characterize conceptual understanding, problem-solving strategies, and errors. In general, successful problem-solving strategies were the same for both novices and experts, including the application of prior knowledge and essential skills to identify the problem concept and execute the correct problem strategy. On the other hand, greater variability was found for the errors exhibited by unsuccessful novice and expert students. The analysis suggests algorithmic heuristics are commonplace, frequently without a deeper conceptual understanding.

Introduction

When confronted with quantitative problems in their General and Analytical Chemistry courses, students often struggle and are unsuccessful. In particular, students often have difficulty solving acid-base equilibria problems that require conceptual knowledge of the topic, mathematical ability, and problem-solving skills. This study aims to evaluate how students, both expert and novice, perform on acid-base equilibria problems by analyzing their problem-solving methods before and after instruction.

Reactions involving acids and bases are, by far, the most extensively discussed class of reaction in introductory chemistry courses. This topic is found repeatedly in both first and second semester General Chemistry, Chemistry 1210 and Chemistry 1220, respectively. Their treatment in "The Central Science," the textbook used in the course investigated in this study, is typical and illustrates the ubiquity of the topic.[6] First semester coverage includes the naming of acids and bases, neutralization reactions, solution stoichiometry and concentrations of solutions, and acid-base reactions and calorimetry. About one-third of the second semester is dedicated to this topic and includes acid-base equilibria, the pH scale, strong and weak acids and bases, acid-base properties of salts, preparing and evaluating buffers, and acid-base titrations. In addition, in both semesters, multiple laboratory experiments address this topic. It is reasonable to conclude that students will struggle in General Chemistry if they have not mastered the topics of acids, bases, neutralization reactions, and their accompanying calculations.

Acids, bases, and buffers are important topics in upper-level chemistry courses as well, including biochemistry courses and organic chemistry courses. The upper-level course that considers the quantitative aspects of this topic most extensively is Analytical Chemistry, Chemistry 2210. Many of the same ideas and skills from General Chemistry are revisited in

Analytical Chemistry, and new ideas, such as activity effects and the need to account for water as a weak acid (or weak base) are introduced. New approaches for solving these problems may also be taught. For example, equilibrium problems, including acid-base equilibria, may be solved using mass balance and charge balance strategies that are not included in General Chemistry. It is not uncommon to find similar, or even identical, algorithmic acid-base questions in both General and Analytical Chemistry courses. It is less common to find comparable conceptual questions in both settings.

The learning objectives and the types of problems found in science courses, including General Chemistry, has evolved over the past few decades based on the proposition that there is a distinction between conceptual understanding and the capacity to carry out algorithmic calculations. As discussed by Holme et al.[13] in their work "Defining Conceptual Understanding in General Chemistry," studies have established that students are often capable of using algorithms to solve numerical problems but may not be able to do so with non-numerical questions about the same content. This has led to an increase in questions involving "visualizing chemistry" in textbooks and on instructor-written tests. The American Chemical Society (ACS) Exams Institute now provides conceptual tests, and their traditional tests include more questions to probe conceptual understanding. Despite this shift in emphasis, as Holme et al.[13] notes, "The definition for conceptual understanding in chemistry has arguably been inferred rather than specified in detail. It is most often viewed relative to some standard (algorithmic problem-solving) that it is not" (p 1477). In an effort to define conceptual understanding, he proposes that a student who demonstrates conceptual understanding can apply core chemistry ideas to situations that are novel to the student (transfer of knowledge), and reason about core chemistry ideas using skills that go beyond mere rote memorization or algorithmic problem-solving (depth of knowledge), as well as executing problem-solving involving critical thinking and translating across scales and representations.

In the current study, the focus is on student performance on algorithmic questions, not conceptual ones. Despite increasing interest in conceptual understanding, the bulk of the questions in textbooks, instructor-written exams, and on ACS exams, involve algorithmic understanding. In this investigation students are *not* asked to transfer ideas to novel situations that are beyond classroom instruction. They are *not* asked to demonstrate a depth of knowledge that exceeds an algorithmic problem-solving approach they may have memorized. This is not to imply that algorithmic questions are easy or simple, but rather that they can be solved by mastering specific skills and strategies that can be identified, practiced, and memorized. This study focuses on understanding student performance on these types of questions.

The centerpiece of science classes is preparing students to correctly answer questions on assessments, and so it is reasonable to find that researchers have sought to understand and improve student problem-solving. This has taken different forms, including generalizable problem-solving approaches, examination of cognitive variables, drawing distinctions between expert and novice approaches, the role of bottom-up reasoning, and the identification of basic essential skills. These are discussed below with respect to this investigation.

Generalizable Problem-Solving

Some researchers have suggested that students have consistently demonstrated a lack of problem-solving ability when asked to solve quantitative problems, and this has led to promotion of generalizable problem-solving strategies to improve performance.[16,18,25] In general, both Okanlawon[21] and Kuo et al.[16] recommend that when first faced with a question, students should qualitatively analyze the prompt to understand the type of question and exactly what the question is asking the student to do. Following that, students must be able to relate the information given in the problem back to their own conceptual understanding of the subject.[17,18,21,25] Students must then be able to connect their conceptual knowledge with their procedural knowledge in order to properly answer the question.

Lorenzo[18] was able to develop a problem-solving heuristic (PSH) to be utilized by students, and 94% of the studied population felt that it assisted in improving their problem-solving abilities. The PSH was based on students drawing a concept map that allowed them to make connections between the information given in the question and their prior knowledge. In addition, Okanlawon's[21] GRASS (Given, Required, Analysis, Solution, Statement) Model can help students find a plausible problem-solving path for quantitative dimensional analysis problems. However, these problem-solving strategies face limitations if a student does not have the appropriate conceptual knowledge base to answer the question.[17,21,25]

The inclusion of generalizable problem-solving strategies in General Chemistry textbooks is varied. Chemistry textbooks include numerous worked examples, and frequently the solutions promote and utilize a consistent strategy. For example, in "Chemistry: The Central Science" the sample exercises use an "Analyze-Plan-Solve-Check" framework.[6] In the textbook "Chemistry" by McMurray et al.[19] the recommended plan is similar, that is "Identify-Strategy-Solution-Check." In the Gilbert et al.[9] textbook "Chemistry" the steps are "Collect, Organize, and Analyze-Solve-Think about it," and in the Atkins et al.[4] textbook "Chemical Principles: The Quest for Insight" the approach is "Anticipate-Plan-Solve-Evaluate." In General Chemistry textbooks like these, a coherent problem-solving framework is provided, especially for algorithmic questions, and although they include common features, it seems as if the authors are intentionally using different terms for the same action, e.g. “check” versus “think about it” versus “evaluate.”

Cognitive Variables

Several cognitive variables have been found to be essential to the problem-solving process. Lee[17] defines five main cognitive variables as specific knowledge, non-specific knowledge, concept relatedness, idea association, and problem translating skills. In their study of high school chemistry students they found that idea association, or the student’s ability to retrieve information when cued by the given information in a question, was the best predictor of a student’s success. Students’ specific knowledge, or knowledge about the question at hand, concept relatedness, and problem translating skills were also essential to students’ ability to be successful. Solaz-Portoles[26] suggests that the cognitive variables essential to problem-solving are prior knowledge, formal reasoning, long-term and working memory, knowledge base, and metacognitive variables. A student’s ability to monitor their own problem-solving process through their metacognition allows a student to evaluate and correct their methods over time, leading to a progressively better problem-solving ability. BouJaude[5] found that students’ formal reasoning, mental capacity and learning orientation can be predictive of their ability to perform well on conceptual chemistry questions. Each of these theories incorporates a student’s prior knowledge base and their ability to integrate the information they are given into their prior knowledge base.

For this study, a valuable idea found in these investigations of cognitive variables is the importance of the learner’s prior knowledge. In Analytical Chemistry, students encounter many of the same topics, and indeed many of the same questions, they had worked with in General

Chemistry. However, General Chemistry is not the first place these students encountered the topics of acids, bases, and pH calculations. These ideas are found in high school courses, and many of the underlying skills, like proportional reasoning and unit conversions, precede their enrollment in General Chemistry as well. Students bring these prior skills, understandings, and misunderstandings with them when they enter into an introductory or an upper-level course.

Expert vs. Novice Problem-Solving

There is a clear distinction between the methods used by experts and the methods used by novices when solving quantitative problems. Petcovic and Libarkin[22] define an expert as "someone who has spent many hours training or solving problems" in their field and is "more capable at solving those problems." Lorenzo[18] differentiates between experts and novices by the amount of knowledge one has and their methods used for problem-solving.

As it pertains to problem-solving, experts are much more likely to correctly analyze and identify the type of question.[16,18] In contrast, novices are more likely to jump to manipulating equations and applying algorithms without first analyzing the question. In addition, experts are able to better interpret and apply theories and models to a given quantitative problem.[18] Experts are able to work forward, working from the given information to connect to the solution while novices tend to work backwards by attempting to connect an unknown solution to the information provided in the question. Finally, novices are more likely to focus on aspects of the questions that are processed quickly, even if these aspects may not be relevant to the question at hand.[11]

Bottom-Up Processes and Heuristics

The role of automatic, bottom-up processes is described by Heckler.[11] As he notes, "The general idea that both bottom-up and top-down mechanisms are at work in learning and answering questions related to physical phenomena is hardly new" (p 229). Heckler focuses on the competition between these mechanisms and proposes that novices often struggle to answer science questions because they are distracted by irrelevant information, or favor information that is more readily processed.

The topic of heuristics is included in Heckler's work, and this is especially relevant for understanding student success (or failure) when completing algorithmic tasks. A heuristic can be viewed as a mental shortcut that eases the cognitive load of making a decision. They are "rules of thumb" that allow someone to make a decision with a limited subset of the available information. In science classes, and in our day to day lives, heuristics are frequently employed because they often lead to a successful (or at least adequate) outcome. Heckler[11] notes that "heuristics tend to be regarded as automatic, bottom-up processes rather than an analytic explicit reasoning process," and they are pertinent for this study because many of the algorithms students use in chemistry courses may be intuitive, automatic heuristics rather than deliberate analyses that incorporate all of the available information (p 247).

Essential Skills

Mikula and Heckler[20] have also investigated student proficiency with essential skills that are prerequisites for completing more complex tasks. Once again, this is a topic that may have an expert vs. novice quality. Essential skills that were investigated among engineering students included tasks like dimensional analysis, using metric prefixes and performing conversions.

These are skills that are automatic for an expert, but a lack of mastery among novices may pose a critical bottleneck, hindering performance. This topic has relevance for a study of algorithmic problem-solving because the algorithms used to solve acid-base equilibria problems are composed of several basic essential skills. In isolation, any of these skills may be relatively straightforward, but to be successful, all of the essential skills must be properly executed.

Model of Chemistry Problem-Solving

Student problem-solving is a multifaceted topic. In their article "College Students Solving Chemistry Problems: A Theoretical Model of Expertise" Taasoobshirazi and Glynn[27] investigate several aspects of the topic and propose a model that is useful for the current study. Having examined research on expert and novice problem-solving, in general and in chemistry, they proposed a model based on ACT-R theory. The ACT-R theory, which stands for *Adaptive Control of Thought Rationale*, is a cognitive theory developed by Anderson and co-workers[1,2] to explain complex behavior in STEM domains. In their study considering novice and expert student performance on chemistry problems involving stoichiometry, thermochemistry, and properties of solutions, Taasoobshirazi and Glynn[27] investigate the relationships between problem conceptualization, self-efficacy, problem strategy, and problem solution (Figure 1). *Problem conceptualization* is an initial step, and it takes place on different scales. For example, chemistry students can readily identify a problem as one involving stoichiometry. Greater expertise is required to identify subcategories, such as accounting for a limiting reactant or calculating the percent yield. *Problem strategy* refers to the work the student does to complete the problem. In their study, all of the problems were calculation-based, so this step included setting up and completing the appropriate mathematical operations. Responses were coded to determine if students used a working-forward or working-backward strategy. *Chemistry self-efficacy* was also investigated, with questions like "I am confident I can do well on chemistry tests" and "I expect to do as well or better than other students in chemistry courses." The final outcome was the *problem solution*.

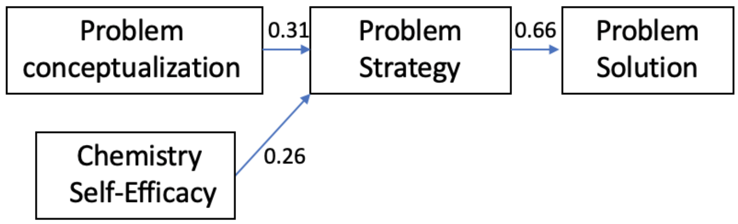


Figure 1: Theoretical model of chemistry problem-solving from Taasoobshirazi and Glynn.[27] Standardized path coefficients shown for a study involving quantitative chemistry problems answered by 101 undergraduate students.

In their data analysis using structural equation modeling, Taasoobshirazi and Glynn[27] determined that the students who conceptualized problems well had high domain-specific self-efficacy, used a working-forward strategy, and had the highest success. In the conceptualization step, successful students could correctly explain their reasoning for placing a question in a particular subcategory and identify similarities and difference among problems. Self-efficacy influenced students' strategy use, as those students with high chemistry self-efficacy seemed to exert effort and persist until they solved the problem. At the problem strategy stage, distinguishing between working-forward and working-backward strategies is noteworthy. Students that used a working-forward strategy were more successful. Generally, a working-forward strategy corresponded to a superior plan that was more efficient and required fewer steps. The authors conclude "We are not stating that working backwards is a bad strategy. We are stating that it is an inefficient strategy for solving quantitative, well-defined problems typically posed in introductory-level chemistry courses. Such problems in areas such as stoichiometry, thermochemistry, and properties of solutions lend themselves to a working-forward strategy because students (and professional chemists) who are knowledgeable and well prepared can apply familiar schemas to the problems" (p 1083).[27] They go on to state that such processes can become "highly automated through guided practice" and become "second nature for knowledgeable students solving such problems" (p 1083).[27] In other words, the authors are describing the acquisition of highly automated strategies suitable for efficiently answering algorithmic quantitative chemistry problems through guided practice.

A working model for the current study is shown in Figure 2. This model expands Taasoobshirazi and Glynn's[27] model to explicitly include the prior knowledge of the student and the additional information they acquire. Although these features are not necessarily absent from the Taasoobshirazi and Glynn's[27] model, they are being emphasized here because this investigation considers possible changes in student performance, both within a class (before and after instruction) and pseudo-longitudinally (introductory and upper-level course). Emphasis is also being given to particular aspects of pre-existing information (*prior knowledge*) and acquired information from instruction (*additional information*), which include the prerequisite essential skills for solving a problem, the bottom-up mechanisms that are present, and, in particular, the heuristics that may be used to answer a question. This working model seeks to combine the Taasoobshirazi and Glynn[27] model (used for describing expert and novice differences in answering algorithmic chemistry questions) with insights from Heckler[11] on the mechanisms individuals use when answering science questions.

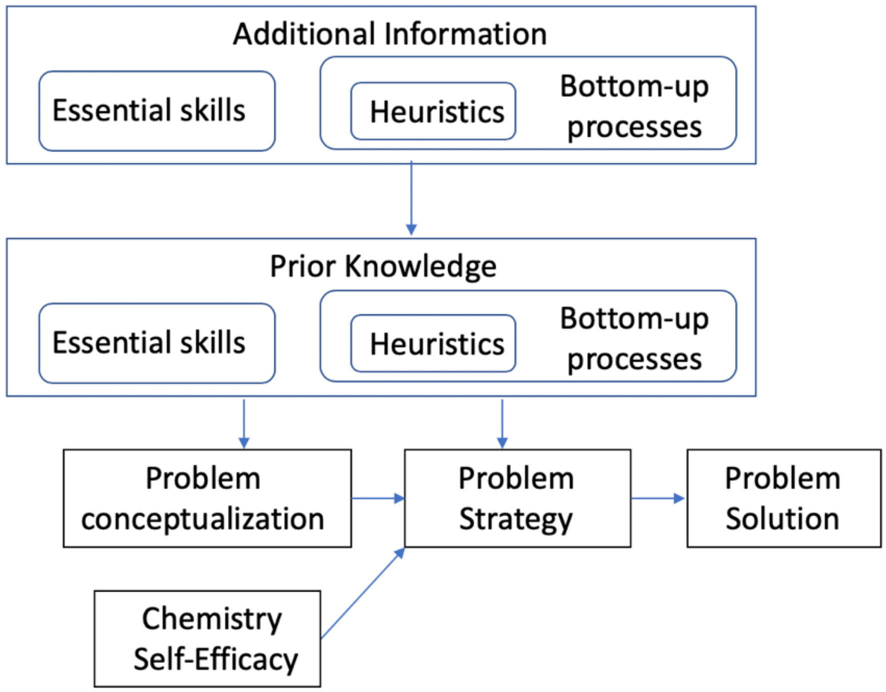


Figure 2: Working model of chemistry problem-solving. In this model, prior knowledge and additional information affect both problem conceptualization and problem strategy.

In this investigation, the working model in Figure 2 will be used to frame analysis of student problem-solving for algorithmic acid-base equilibrium questions. Chemistry self-efficacy, although a contributing factor, will not be examined in this study. Inferences will be drawn by examining student work to identify differences in what successful and unsuccessful students do when answering these questions.

Methods

Second semester General Chemistry students in Chemistry 1220 (n=169) and Analytical Chemistry students in Chemistry 2210 (n=34) at a Midwestern research university were given an open-response instrument both before and after instruction in order to gain insight into their fluency with, and approaches for, answering algorithmic quantitative questions. Students in both courses were assigned to either an Acid Version (n=76) or a Base Version (n=127) of the instrument and completed the same version before and after classroom instruction (Figure 3). General Chemistry is a prerequisite for Analytical Chemistry. This is a longitudinal study within a given course, and a pseudo-longitudinal one that includes different students in an introductory course and an upper-level course.

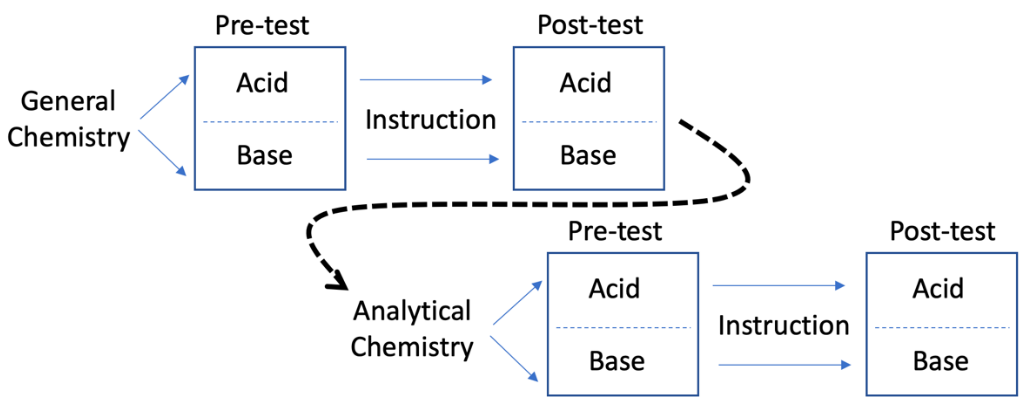


Figure 3: Overview of project design.

Comparable Acid and Base Versions of the survey instrument were written, each composed of five questions pertaining to strong electrolytes, weak electrolytes, neutralization reactions, and titrations (Table 1). All questions are representative of quantitative acid-base problems found in second semester General Chemistry courses. Several questions intentionally included dibasic or diprotic strong electrolytes, cf. Question 1 (base), Question 4 (acid and base).

Surveys were administered in class recitations or lab periods and students were given approximately 30 minutes to answer all the questions. Students were asked to show their work, and they were allowed to use a calculator.

Description	Acid Version	Base Version
1. Strong electrolyte	Calculate the pH of 0.025 M HI.	Calculate the pH of 0.025 M $Sr(OH)_2$.
2. Weak electrolyte	Calculate the pH of 2.0 M HF. K_a for HF = 6.6x10^{-4}	Calculate the pH of 2.0 M CH_3NH_2. K_b for CH_3NH_2 = 4.38x10^{-4}
3. Salt	Calculate the pH of 0.25 M NH_4Cl. K_b for NH_3 = 1.8x10^{-5}	Calculate the pH of 0.25 M NaF. K_a for HF = 6.6 x 10-4
4. Neutralization	How many mL of 0.20 M KOH are needed to neutralize 150 mL of 0.020 M H_2SO_4?	How many mL of 0.20 M HCl are needed to neutralize 150 mL of 0.020 M $Ca(OH)_2$?
5. Titration, excess strong electrolyte	If 25.0 mL of 0.25 M HNO_3 is combined with 15.0 mL of 0.25 M CH_3NH_2, what is the pH? K_b for CH_3NH_2 = 4.38x10^{-4}	If 25.0 mL of 0.25 M NaOH is combined with 15.0 mL of 0.25 M CH_3COOH, what is the pH? K_a for CH_3COOH = 1.8x10^{-5}

Table 1: Description of Acid and Base Survey Instruments.

Coding of the open-response data included several steps. First, responses were tallied as correct or incorrect. Normalized gains were calculated using Equation 1:

$$\text{Normalized Gain} = (\text{Post \%} - \text{Pre \%}) / (100 - \text{Pre\%}) \quad \text{(Equation 1)}$$

Next, the responses were treated qualitatively to identify emergent themes in the student work. Coding was done for each question, and for each version of the survey. This was an iterative process as some themes were merged together and others were discovered. Certain themes were particular to a specific question, whereas others were common across multiple questions. Dependency of the success on one question with another was assessed using cross tabulations. This type of table was also used to gauge the effectiveness of writing an equilibrium question on student success in Question 3 and on student success between two different problem-solving approaches in Question 4.

Instruction in General Chemistry included six fifty-five minute lectures, three laboratory experiments, video content recorded by the instructor, homework assignments using the program Mastering Chemistry and recitation assignments. The lectures covered acid-base equilibria topics including strong electrolytes, weak electrolytes, the pH scale, neutralization reactions, the autoionization of water, the pH of salt solutions, buffers, and titrations. Students also saw demonstrations during lecture as well as practiced example problems. The laboratory experiments focused on the acid-base properties of salt solutions, the titration of strong acids and bases, and the titration of weak acids and bases.

Instruction in Analytical Chemistry included nine fifty-five minute lectures and three laboratory experiments. These lectures discussed acid-base equilibria in more detail than in General Chemistry and included the topics of conjugate acid-base pairs, dissociation constants, autoionization of water, activity calculations, fraction of dissociation, buffers, polyprotic acids, polyprotic buffers, the pH of salt solutions, monoprotic titrations, and polyprotic titrations. The laboratory experiments focused on preparing a standard base, identifying a weak acid, and incorporating activity coefficients into calculating the pH of a buffer solution. In comparison to the General Chemistry course, more time was spent discussing the autoionization of water, activity coefficients, and polyprotic acids. However, the lecture styles for each course were similar in nature as the instructor for both courses utilized slideshows intermixed with example problems to present the material.

For the purposes of this study, the General Chemistry students are considered novices in the subject of acid-base equilibria while the Analytical Chemistry students are considered experts. In addition to having already passed the General Chemistry course, the Analytical Chemistry students also spent more time in lecture on the subject, allowing them more time to develop their expertise.[22]

Results and Discussion

Overall Performance Analysis

The summary of correct and incorrect responses for both survey instruments in both classes, pre- and post-test, is shown in Table 2. Columns Q1, Q2, etc. indicate number the correct/total number. As an example, for the Chemistry 1220 students, 26/60 were correct on Question 1 of the pre-test, and this improved to 54/60 on the post-test. The combined acid and base scores are included in Table 3 as calculated percentages, along with the normalized gain for the pre to post scores.

		Q1	Crosstabs Q2			Q2	Crosstabs Q3			Q3	Q4	Crosstabs Q5			Q5
ACID	Pre	26/60 **43%**	Q1	34 **57%**	0 **0%**	5/60 **8%**	Q2	55 **92%**	0 **0%**	0/60 **0%**	7/60 **12%**	Q4	53 **88%**	0 **0%**	0/60 **0%**
1220				21 **35%**	5 **8%**			5 **8%**	0 **0%**				7 **12%**	0 **0%**	
	Post	54/60 **90%**	Q1	4 **7%**	2 **3%**	35/60 **58%**	Q2	23 **39%**	2 **3%**	19/60 **32%**	14/60 **23%**	Q4	41 **68%**	5 **8%**	11/60 **18%**
				21 **35%**	33 **55%**			18 **30%**	17 **28%**				8 **13%**	6 **10%**	
2210	Pre	5/16 **31%**	Q1	11 **69%**	0 **0%**	1/16 **6%**	Q2	15 **94%**	0 **0%**	1/16 **6%**	4/16 **25%**	Q4	12 **75%**	0 **0%**	0/16 **0%**
				4 **25%**	1 **6%**			0 **0%**	1 **6%**				4 **25%**	0 **0%**	
	Post	16/16 **100%**	Q1	0 **0%**	0 **0%**	11/16 **69%**	Q2	3 **19%**	2 **12%**	6/16 **38%**	7/16 **44%**	Q4	9 **56%**	0 **0%**	0/16 **0%**
				5 **31%**	11 **69%**			7 **44%**	4 **25%**				7 **44%**	0 **0%**	
BASE	Pre	13/110 **12%**	Q1	96 **87%**	1 **1%**	1/110 **1%**	Q2	108 **98%**	1 **1%**	1/110 **1%**	27/110 **25%**	Q4	83 **75%**	0 **0%**	1/110 **1%**
1220				13 **12%**	0 **0%**			1 **1%**	0 **0%**				26 **24%**	1 **1%**	
	Post	77/109 **71%**	Q1	27 25%	5 4%	48/109 **44%**	Q2	54 **50%**	7 **6%**	33/109 **30%**	53/109 **49%**	Q4	43 **39%**	13 **12%**	35/109 **32%**
				34 **32%**	43 **39%**			22 **20%**	26 **24%**				31 **28%**	22 **20%**	
2210	Pre	7/18 **39%**	Q1	10 **56%**	1 **6%**	4/18 **22%**	Q2	14 **78%**	0 **0%**	4/18 **22%**	10/18 **56%**	Q4	7 **38%**	1 **6%**	3/18 **16%**
				4 **22%**	3 **16%**			0 **0%**	4 **22%**				8 **44%**	2 **12%**	
	Post	13/18 **72%**	Q1	1 **6%**	4 **22%**	16/18 **89%**	Q2	1 **6%**	1 **6%**	13/18 **72%**	11/18 **61%**	Q4	5 **28%**	2 **12%**	7/18 **38%**
				1 **6%**	12 **66%**			4 **22%**	12 **66%**				6 **33%**	5 **28%**	

Table 2: Summary of correct and incorrect responses for General Chemistry (1220) and Analytical (2210) students. Crosstabs are for paired Questions 1 and 2, Questions 2 and 3, and Questions 4 and 5.

Course		Q1: Strong Electrolyte	Q2: Weak Electrolyte	Q3: Salt	Q4: Neutralization	Q5: Excess Strong Electrolyte
General Chemistry (n=169)	Pre	23%	4%	1%	20%	1%
	Post	78%	49%	31%	40%	27%
	Gain	**0.71**	**0.47**	**0.30**	**0.24**	**0.27**
Analytical Chemistry (n=34)	Pre	35%	15%	15%	41%	9%
	Post	85%	79%	56%	53%	21%
	Gain	**0.77**	**0.76**	**0.48**	**0.20**	**0.13**

Table 3: The percentage of successful students and normalized gains from before and after instruction on each question.

For both courses there were strong normalized gains made from before instruction to after instruction. This is especially apparent in Question 1, where students in both courses demonstrated normalized gains of over 0.70. Students also demonstrated significant improvement on Question 2, with the General Chemistry students demonstrating a gain of 0.47 while the Analytical Chemistry students demonstrated a gain of 0.76. As would be expected, for all questions from both testing periods, the expert students outperformed the novice students, with one exception: Question 5 post-test (Figure 4).

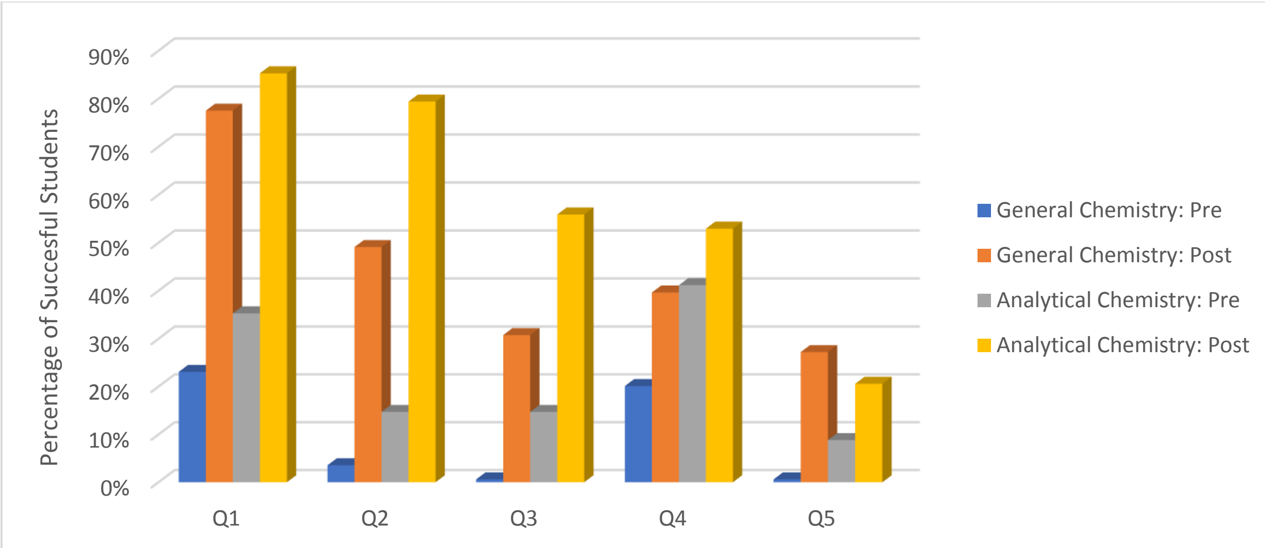


Figure 4: Performance of General and Analytical Chemistry students before and after instruction.

In absolute terms, the pre-test scores are low. For the General Chemistry students, the pre-test scores range from 1% to 23%. Although the gains are significant for these students, Question 1 is the only question in which the average score exceeds 50%. Most of the General Chemistry students' understanding of acids and bases comes from their learning in high school as well as topics covered in the first semester General Chemistry course (Chemistry 1210) such as neutralization reactions. High school students' difficulty in understanding acid-base concepts and solving acid-base problems is well documented.[3] The low pre-test scores of General Chemistry students observed here further confirms this difficulty in understanding. The pre-test scores were higher for the Analytical Chemistry students, but also in a low range (9% to 41%). Only the post-test scores for the Analytical Chemistry students have several questions scoring above 50%.

Longitudinally, there is a notable gap between student performance at the end of General Chemistry and student performance at the beginning of Analytical Chemistry. For almost all of the questions, the Analytical Chemistry students before instruction perform more similarly to their General Chemistry counterparts *before* instruction rather than General Chemistry students *after* instruction. Question 1 (the highest scoring question) illustrates this point. The Analytical Chemistry pre-test score of 35% is much closer to the General Chemistry pre-test score than the General Chemistry post-score, at 23% and 78% respectively. This result should be unsurprising given that previous research has shown that there is a decrease in achievement on questions on a given topic during the first 48 hours following a test.[7] It has been shown that interventions such as repeated recall test can be employed to overcome the decrease in achievement.[28]

Table 2 also includes cross tabulation data for three sets of questions (Question 1 & Question 2, Question 2 & Question 3, Question 4 & Question 5). The cross tabulations summarize whether students were correct on both questions, incorrect on both, or another combination. The first row or column correspond to the number of incorrect responses while the second row or column corresponds to the number of correct responses. Consider the cross tabulation data for Question 1 and Question 2 on the pre-test for General Chemistry students. Overall, 26/60 students were correct on Question 1, and 5/60 were correct on Question 2. The cross tabulation provides additional information: 34 students were incorrect on both Question 1 and Question 2, no student was correct on Question 2 without being correct on Question 1, 21/26 students were correct on Question 1 but not Question 2, and 5/26 students were correct on both Question 1 and Question 2. Cross tabulations are a simple way to explore hierarchies of skills, and these sets of questions were chosen due to the underlying skills they contain.[29]

Questions 1-3 were written to encompass a progression of essential skills and increase in complexity, moving from a strong electrolyte, to a weak electrolyte, and then a salt. The most meaningful cross tabulation comparisons are from the General Chemistry post-tests; the pre-tests are uniformly low scoring and the Analytical Chemistry results have a smaller sample size.

Turning to the General Chemistry post-test results, cross tabulation data show that correctly answering Question 1 (strong electrolyte) is necessary for answering Question 2 (weak electrolyte). For the Acid Version, in 33/35 cases (94%), students correct on Question 2 had been correct on Question 1. For the Base Version, in 43/48 cases (90%), students correct on Question 2 had been correct on Question 1. To correctly answer the weak electrolyte question, a student must first be able to answer the strong electrolyte question. There are very few counterexamples. The cross tabulation results for Question 2 (weak electrolyte) and Question 3 (salt) lead to a similar finding. For the Acid Version (17/19 cases, 90%) and the Base Version (26/33 cases, 79%), to correctly answer the salt question, a student must first be able to answer the weak electrolyte question.

Questions 4 and 5 both involve neutralization reactions and the combining of an acid and a base. An interesting finding from the cross tabulation analysis is the relatively weak hierarchical relationship for these two questions. The objective in Question 4 is to determine the volume of acid necessary to neutralize a basic solution (or vice versa), and a similar calculation is also an initial step in the problem-solving strategy for answering Question 5. For the Base Version, in 22/35 cases (63%) to correctly answer Question 5, a student must first answer Question 4. This is noteworthy because, unlike the other cross tabulation analyses, there are a significant number of counterexamples. More than one-third of the students correctly answered Question 5 while incorrectly responding to a question based on a (presumably) prerequisite skill.

Key findings

- Pre-test scores are low in both Chemistry 1220 and 2210 for all topics.

- Pre-test scores in Chemistry 2210 are more comparable to the Chemistry 1220 pre-test than the 1220 post-test for Question 1 and Question 2.
- Upper-level students scored lower on Question 5 after instruction compared with General Chemistry students.
- Normalized gains are very high for Question 1 and Question 2 for both Chemistry 1220 and 2210.
- An anticipated performance hierarchy is evident for Questions 1,2, and 3.
- The anticipated performance hierarchy for Question 4 and Question 5 is weaker than anticipated.

Individual Question Analysis

Whether students correctly or incorrectly answered a question is informative. Additional insights are gained by comparing the overall performance in various ways: General Chemistry versus Analytical Chemistry, pre- versus post-test, Acid Version versus Base Version, etc., and by investigating hierarchical relationships. However, these analyses provide limited information on the problem-solving strategies employed by the students and what does, or does not, lead to success. Analysis of overall performance data raised several interesting questions. Why do the upper-level students perform more poorly on the most advanced question (Question 5)? Why is there a relatively weak hierarchical relationship between Question 4 and Question 5? Can prerequisite essential skills be identified? To address questions like these, qualitative analysis of individual responses is essential.

Question 1: Calculation of pH for an acid or base strong electrolyte

Using concentration information to calculate the pH of an acid or base solution is a task found in all General Chemistry textbooks, and that is what Question 1 examines (Table 1). The Acid Version and the Base Version differ in several respects, beyond simply identifying HI as an acid and $Sr(OH)_2$ as a base. As shown in the worked solutions (Appendix A), the Base Version requires additional steps to report pH having first found pOH or $[OH^-]$. Also, the Base Version includes a strong electrolyte that dissociates to produce two $OH^-_{(aq)}$ per formula unit, whereas the Acid Version dissociates to produce one $H^+_{(aq)}$ per formula unit.

In the working model of chemistry problem-solving (Figure 2), *problem conceptualization* involves categorizing Question 1 as involving an acid or base strong electrolyte. For the Base Version, an additional step is identifying the stoichiometry of the dissociation. *Essential skills* include having memorized strong acids and strong bases, knowing how strong electrolytes dissociate, calculating ion concentration in a solution having accounted for dissociation, using a calculator to find pH from $[H^+]$, and, for the Base Version, converting between $[OH^-]$ and $[H^+]$ or between pOH and pH. The subsequent *problem strategy* has little flexibility or branch points in which the student makes a decision beyond the manner in which $[OH^-]$ leads to a reported pH.

All of the students in Analytical Chemistry, and the majority of students in General Chemistry, had the opportunity to develop sufficient *prior knowledge* to answer Question 1. This is a familiar question, commonplace in the high school curriculum, and certainly present in General Chemistry courses. It is therefore noteworthy to find students in both classes performing poorly on the pre-tests. As shown in the overall results, many students in General Chemistry and Analytical Chemistry were successful on Question 1 in the Acid Version, the question that students were most likely to have seen in previous chemistry classes. Since many students already had these essential skills as *prior knowledge*, there was not much to be gained as *additional information* through instruction. Some General Chemistry students who may not have seen this content before would have incorporated these skills into their additional information, but the rest of the General Chemistry students and the entirety of the Analytical Chemistry students should have already held these skills as *prior knowledge*.

The test included the prompts to “Show your supporting work” and “If you do not know how to answer a question, please identify parts of the question you do understand.” For Question 1, this resulted in most students writing information of some kind. For the General Chemistry students there were three broad categories of responses for the unsuccessful students. One group of students responded with comments but did not attempt to answer the question. Statements included things like “Don’t know,” “IDK,” “I haven’t learned any of this yet,” and question marks. These students are failing at the *problem conceptualization* stage, or if they identified the nature of the problem, they did not have a problem strategy to implement.

Another group attempted to solve the problem, often by restating the provided information, and then manipulating it in various ways (Figure 5). In these cases, it is interesting to see what information students seek to use when answering what is an algorithmic question. Many students restated the concentration information and converted molarity to moles per liter, but then did odd things with this information, such as using Avogadro’s number to determine the number of ions. These students have some success with *problem conceptualization* and display some *essential skills* necessary for answering the question; however, they lack a *problem strategy* because they do not recall the appropriate practiced algorithm from their prior knowledge.

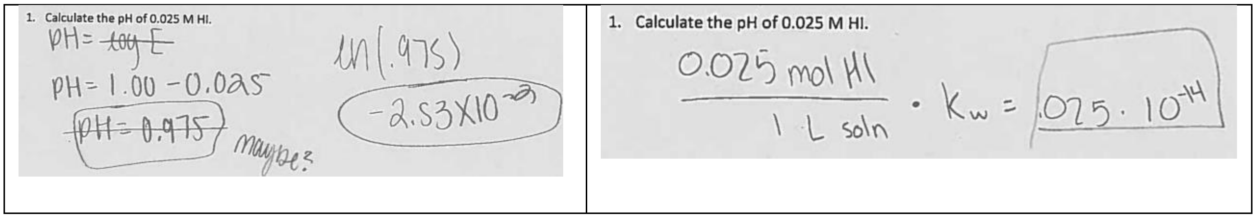


Figure 5: Pre-test responses for General Chemistry students on Question 1. In these examples, students manipulate the provided information but do not utilize the standard algorithmic approach and are unsuccessful.

The third group of unsuccessful General Chemistry students lacked the specific essential skill of understanding pH notation and converting from concentration to pH (Figure 6). In several respects, these students are close to being successful. They seem able to conceptualize the problem and have a partial strategy, but they are unable to recall the definition of pH from their prior knowledge.

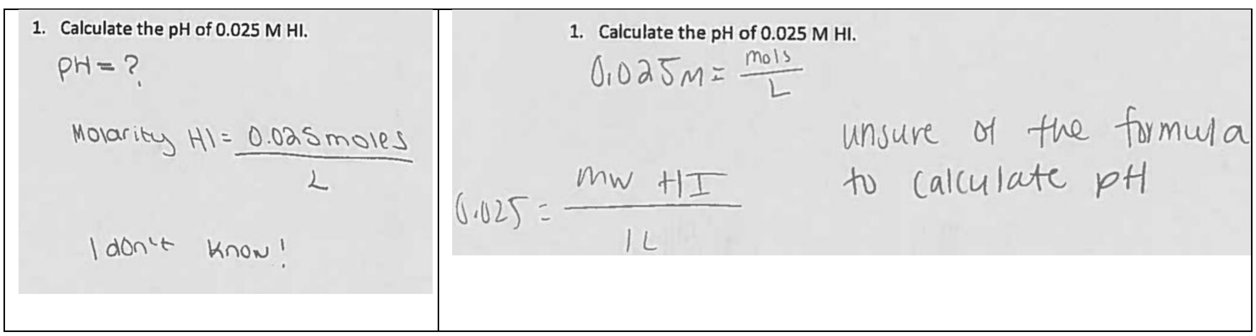


Figure 6: Pre-test responses for General Chemistry students on Question 1 that are unable to calculate pH.

The prior knowledge for Analytical Chemistry students is more well-defined than General Chemistry students because it is known these upper-level students completed the introductory course. At one time, all of these students *must* have been able to answers questions like this one if they passed General Chemistry. For the Analytical Chemistry students, there were once again three broad categories of responses from the unsuccessful students, but these differ slightly from those of the General Chemistry students. In the first group were students that provided comments but no work. These included statements like "I know this is a simple calculation, just too rusty to remember the formula ☹," or "I took gen. chem. 2 ~ 4 years ago. I know at one point I could do this but I definitely don't remember now." Unlike General Chemistry students, these responses indicate an awareness of having this information at one time in their prior knowledge skill set. The next group included students that unsuccessfully manipulated the provided information and did not employ a standard algorithm. The final group's shown work included algorithms for acid-base calculations that were not applicable for this question (Figure 7). Examples of this kind were not common among General Chemistry students, but they are found among upper-level students. These students seem to be recalling and misapplying *heuristics* that are applicable for different acid-base calculations. Two of the most prevalent heuristics used in General Chemistry to solve acid-base problems include Initial-Change-Equilibrium (ICE) tables for questions involving equilibrium and the Henderson-Hasselbalch equation for questions involving buffers. These heuristics were present in the prior knowledge of the upper-level students, and incorrectly applied for Question 1.

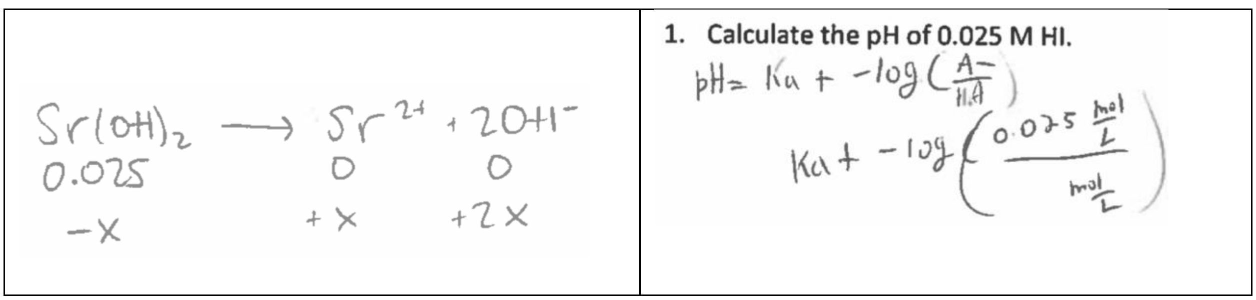


Figure 7: Pre-test responses for Analytical Chemistry students on Question 1 that utilized inappropriate heuristics, such as an ICE table (left), and the Henderson-Hasselbalch equation (right).

Turning to the post-test results for Analytical and General Chemistry students for Question 1, two themes emerge: Students in both classes showed large gains, and the Acid Version was easier than the Base Version. There was little to be learned from the qualitative analysis of post-test responses for the successful students beyond the fact that they employed the same strategy. The worked solution in Appendix A describes the standard algorithmic problem-solving strategy, and this is the strategy that successful students employed.

As described above, the Base Version of Question 1 is more complex for two reasons: the need to account for the stoichiometry of the dissociation, and the need to convert from $[OH^-]$ to pH. To determine the importance of these factors, qualitative data were used and student errors were identified. This indicated that the primary difficulty students encountered with the Base Version was with the dissociation stoichiometry. On the General Chemistry post-test, 90% of students were successful with the Acid Version while only 71% were successful with the Base Version. If one allows for an error in dissociation (i.e. it is the only error present), success on the Base Version reaches 85%. There were few examples of errors converting to pH from $[OH^-]$.

There are a number of possibilities as to why students would consistently fail to account for the stoichiometry of the base dissociation. It is possible that students simply miss the subscript or do not notice it is present. Perhaps students do not understand that the subscript is relevant to concentration calculations. While we cannot conclusively determine the cause, students' struggles with recognizing dissociation from a symbolic representation is well documented.[15,24] These struggles are thought to arise from students' misunderstandings of the relationship between the symbolic and molecular representation of reactions. Recent work has recommended that instructors make clear connections between the macroscopic, molecular, and symbolic representations of reactions (these representations are often referred to as the Johnstone triangle).[14]

In the working model of chemistry problem-solving (Figure 2), how should an error in dissociation be accounted for? It could involve *problem conceptualization* and not identifying the correct subcategory. Another contributing factor could be a *bottom-up mechanism* in which the student uses the most accessible information, that is the concentration for a basic solution, and proceeds with the calculation without pausing to analyze the nature of the dissociation. Less likely is the possibility that students lack the essential skill of understanding how $Sr(OH)_2$ dissociates.

Key findings for Question 1.

- On pre-tests, unsuccessful General Chemistry students 1) included statements of not knowing, 2) manipulated provided information, 3) did not understand the pH convention.
- On pre-tests, unsuccessful Analytical Chemistry students 1) included statements of not remembering, 2) manipulated provided information, 3) misapplied heuristics, such as using ICE tables and the Henderson-Hasselbalch equation.
- Successful students on the post-test used the same problem strategy and employed the same memorized algorithm.
- Post-test scores were much higher, with the Acid Version scoring higher than the Base Version. This is attributed to difficulty accounting for the dissociation of $Sr(OH)_2$. This may be understood as a failure of problem conceptualization that may be influenced by a bottom-up mechanism.
- An instructional implication is to recognize introductory and upper-level students both have gaps in their prior knowledge. For General Chemistry students, this includes the concept of pH. For Analytical Chemistry students, this includes heuristics retained from earlier courses that are misapplied. Following instruction, these shortcomings are diminished, but problem conceptualization remains a concern when dealing with diprotic or dibasic substances like $Sr(OH)_2$.

Question 2: Calculation of pH for an acid or base weak electrolyte

Question 3: Calculation of pH for a salt

Equilibrium calculations are an important topic in Chemistry 1220 and Chemistry 2210. Acid-base equilibria and the calculation of the pH for a weak acid or a weak base is examined in Question 2, and the closely related equilibrium calculation for the pH of a salt is examined in Question 3 (see Table 1). The Acid Version and the Base Versions are very similar for each question, with the primary difference being the need to convert from $[OH^-]$ to pH, as shown in the worked solution (Appendix A).

In the working model of chemistry problem-solving for Question 2, *problem conceptualization* entails pH determination for a weak acid or weak base. *Essential skills* include being able to identify weak acid and bases from a formula when paired with K_a or K_b information, writing the appropriate K_a or K_b equilibrium expression, writing and using an ICE table, and for the Base Version, converting between $[OH^-]$ and $[H^+]$ or between pOH and pH. Like other algorithmic problems, the *problem strategy* is rigid and involves little decision making.

Problem-solving for Question 3 includes a *problem conceptualization* stage in which the acid-base characteristics of a salt is recognized. *Essential skills* are similar to those for Question 2, but include the identification of the salt and, most significantly, writing the K_a or K_b equilibrium expression for the conjugate acid or conjugate base that is present. Although Question 3 is best described as an algorithmic problem with a pre-defined approach, the *problem strategy* is one of the more complex in General Chemistry.

The *prior knowledge* for General Chemistry students for both questions is expected to be low, whereas all of the Analytical Chemistry students would have experience with these problems from prior coursework. Among this prior knowledge is the *heuristic* of using an ICE table. Over the instructional period, the General Chemistry students should have incorporated the ICE table heuristic and essential skills relating to writing equilibrium expressions into their *additional knowledge,* allowing for a considerable gain in success from before to after instruction.

As noted above, the gains with instruction for Question 2 are very significant. Scores for the General Chemistry students improve from 4% to 49% (normalized gain of 0.47), and scores for Analytical Chemistry students improve from 15% to 79% (normalized gain of 0.76). The Acid Version and the Base Version are intended to be equivalent, and the scores for each were similar. The gains following instruction for Question 3 are significant, but smaller than those for Question 2. The overall results also indicated a hierarchical relationship among Questions 1, 2 and 3. This was expected given the common essential skills and clear increase in complexity.

The qualitative response data from the pre-tests for these questions were not very useful as little was written and students struggled with problem conceptualization, did not understand symbols, and lacked a problem strategy. Statements like “I don’t know” and “I haven’t learned any of this” were common. As found for Question 1, some General Chemistry students again used the provided information and manipulated it unsuccessfully (Figure 8). It is interesting to observe the mathematical operations the students use when grasping for a problem strategy, such as multiplying concentration with K_a, or calculating the natural logarithm of K_b.

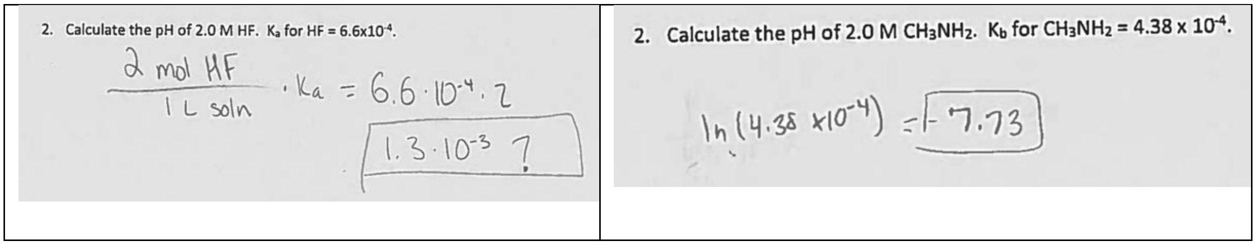
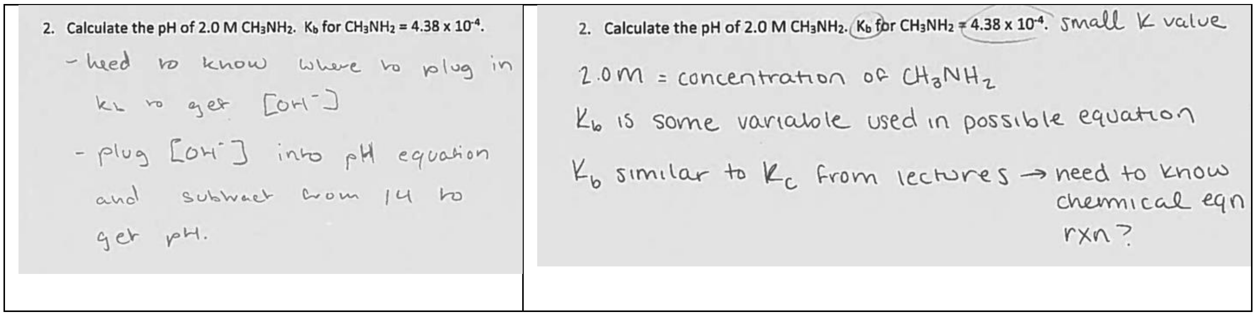


Figure 8: Pre-test responses for General Chemistry students on Question 2. In these examples, students manipulate the provided information but do not utilize the standard algorithmic approach and are unsuccessful.

A key stumbling block for General Chemistry students was understanding the symbol K_b, the equilibrium constant for a weak base. At this point in the semester students had been introduced to the concept of equilibrium but had not yet learned how it applied to the equilibrium of weak acid and weak bases. Some students specifically raise this point, stating, "I don't understand K_b." Other students provide far greater insights into their problem strategy by stating what they do and do not know. In the example on the left in Figure 9, the student describes a strategy for finishing the problem ("plug [OH-] into pH equation and subtract from 14 to get pH"), recognizes that K_b will be used to determine [OH_-], but does not know how to accomplish this task. The example on the right in Figure 9 also illustrates a student that understands some of the ideas, but does not understand K_b. In this case the student is making connections with ideas involving equilibrium, considers the size of the K_b value, and asks "K_b similar to K_c from lecture → need to know chemical eqn rxn?" These are remarkable snapshots of students sharing their problem strategy. These students correctly conceptualize the problem despite having not yet learned an essential skill to complete the task, but have the metacognitive awareness to reflect on their problem strategy and identify the gap in their thought process.


2. Calculate the pH of 2.0 M CH_3NH_2. K_b for CH_3NH_2 = 4.38×10^{-4}.

- need to know where to plug in kb to get [OH^-]
- plug [OH^-] into pH equation and subtract from 14 to get pH.

2. Calculate the pH of 2.0 M CH_3NH_2. K_b for CH_3NH_2 = 4.38×10^{-4}. small K value

2.0 M = concentration of CH_3NH_2

K_b is some variable used in possible equation

K_b similar to K_c from lectures → need to know chemical eqn rxn?

Figure 9: Pre-test responses for General Chemistry students on Question 2. In these examples, students describe the parts of the question they understand and how they do not understand how to use K_b to determine [OH^-].

The upper-level students have greater prior knowledge, and their pre-tests included examples in which the standard algorithm was executed successfully (Figure 10, left). There were not examples in which an alternative problem strategy led to success; the successful students appeared to recall and apply the appropriate heuristic, an ICE table. Significantly, a similar problem strategy was used by many upper-level unsuccessful students. These students used K_w to find K_a and find the negative log of this value, leading to a reported value of about 10.6 (Figure 10, right). This is noteworthy for several reasons. First, this question is activating similar features in the prior knowledge of many students, and they are recalling information and performing the same essential skills. This is occurring not for just one step, but for several in combination. Secondly, this particular problem strategy does not work because it ignores the concentration of the solution and therefore is not appropriate for any acid-base equilibrium problem. This is not the case of students misapplying a heuristic. Rather, they are recalling the same two essential skills, applying them, and finding an answer that is reasonable for the pH of a basic solution.

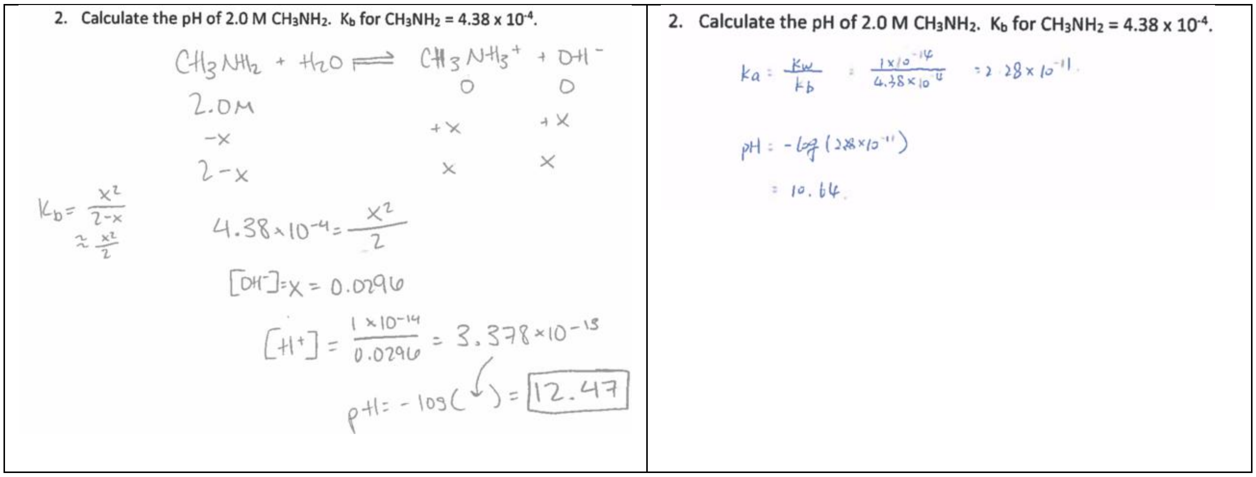


Figure 10: Pre-test responses for Question 2 by a successful Analytical Chemistry student (left) and an Analytical Chemistry student demonstrating a common flawed problem strategy (right).

As for the post-tests, students in both classes dramatically improve from before to after instruction. There are not multiple pathways that lead to the correct answer, and successful students use the same problem strategy. It is also clear that incorrect problem strategies include many essential skills and the heuristics of an ICE table and the Henderson-Hasselbalch equation, but these heuristics are not used as a part of a coherent framework, are misapplied, and do not correspond to the equilibrium present in the reaction. In many examples, a given student uses the same flawed problem strategy for Questions 2 and 3. These questions are closely related, and these students seem to successfully negotiate aspects of problem conceptualization, but then have a flawed, but reproducible, problem strategy that is then applied to both questions. Consider the responses shown in Figure 11 for the post-test of the same student. This student conceptualizes the problem as one involving equilibrium. Their problem strategy incorporates many essential skills, involving setting up an ICE table, writing an equilibrium expression, solving for “x”, and taking the negative log of x to find pH. The strategies are the same, but both are victim to the same error, which is starting the process with an incorrect equilibrium reaction. In Question 2, the student has treated CH_3NH_2 as a weak acid instead of a weak base and set up the ICE table to solve for H_3O^+. In Question 3, the student has placed NaF in equilibrium with F^- instead of writing an equilibrium expression that treats F^- as a weak base.

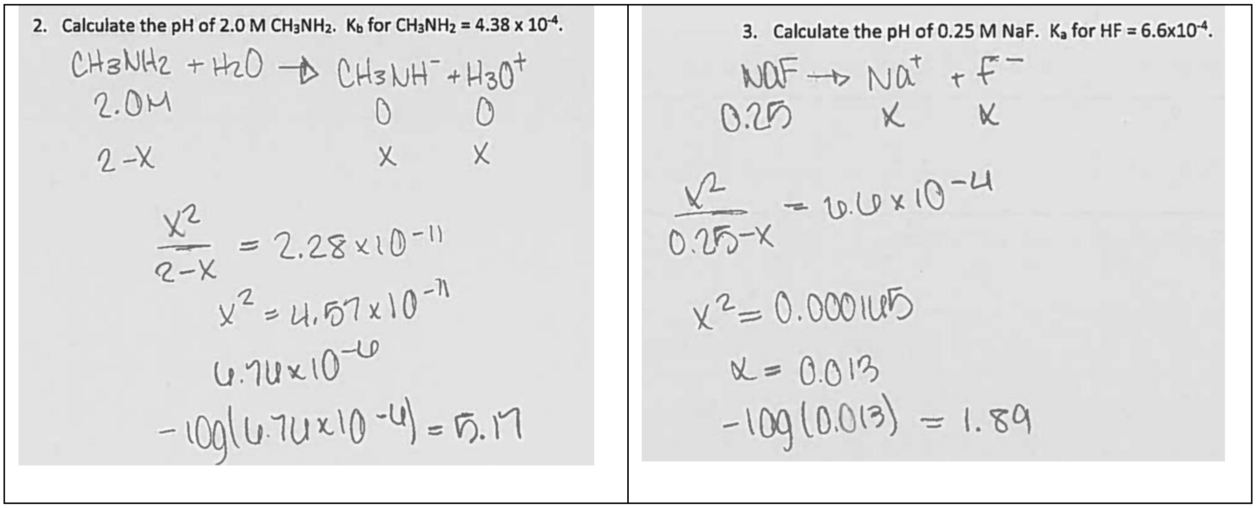


Figure 11: Post-test responses for the same General Chemistry student on Questions 2 and 3.

Both Analytical and General Chemistry students struggled with writing the correct equilibrium equation, and Analytical Chemistry students (31%) were twice as likely to make this mistake than the General Chemistry students (15%) (Figure 12). Students in both courses also attempted to use the Henderson-Hasselbalch (H-H) equation, which is an inappropriate use of this heuristic. The Henderson-Hasselbalch equation is an example of an algorithmic heuristic that was incorporated into the students' *additional knowledge* over the course of instruction, and students seem to turn to when they are not sure what to do. Choosing to use the Henderson-Hasselbalch equation demonstrates that students were unable to recognize the concept (finding the pH of the salt solution) and therefore deferred to a simple, but inappropriate, problem-solving method.

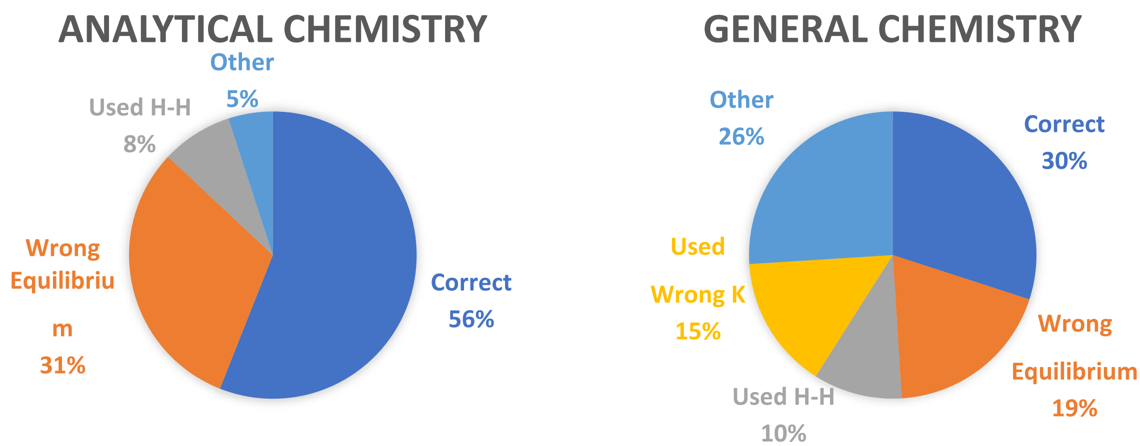


Figure 12: Strategies used by students in both courses on Question 3 after instruction. Common errors include writing the wrong equilibrium, using the Henderson-Hasselbalch equation (H-H), or using the incorrect dissociation constant (Wrong K). Other errors included calculation mistakes or no response.

General Chemistry students often made the mistake of using the incorrect dissociation constant, K. This includes using the K_a value when the K_b value should have been used and vice versa. The General Chemistry students were also more prone to being unsuccessful (26%) in other ways, such as calculation mistakes or simply not responding, than the Analytical Chemistry students were (5%).

When comparing student success on the Acid Version of Question 3 with that of the Base Version of the question, there are some differences between the Analytical and General Chemistry student performance. Most notably, Analytical Chemistry students were more than twice as successful on the Base Version of the question, whereas the General Chemistry students had about the same level of success on the both versions of the question. The primary conclusion is that upper-level students are more successful on a Base Version than they are on an Acid Version because they are more capable writing an equilibrium expression using $F^-_{(aq)}$ than with $NH_4^+{}_{(aq)}$.

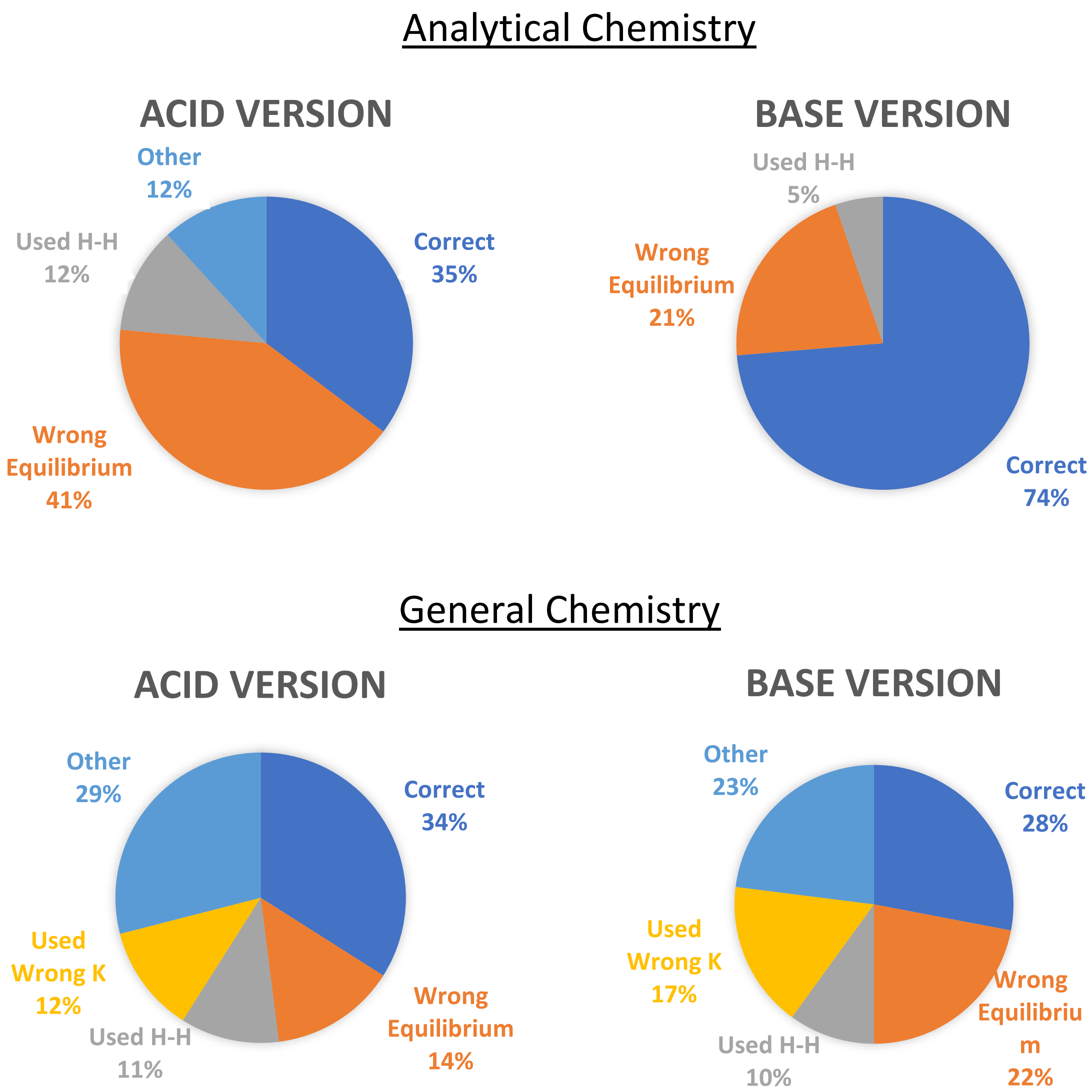


Figure 13: Strategies used by students on the Acid and Base Versions of Question 3 after instruction. Common errors include using the wrong equilibrium, using the Henderson-Hasselbalch equation (H-H), or using the incorrect dissociation constant (Wrong K). Other errors included calculation mistakes or no response.

	Analytical Chemistry			General Chemistry	
pre=	Answered Successfully	Answered Unsuccessfully		Answered Successfully	Answered Unsuccessfully
No reaction shown	1 (3%)	5 (14%)	No reaction shown	8 (4%)	58 (32%)
Incorrect reaction	2 (6%)	10 (28%)	Incorrect reaction	6 (3%)	30 (17%)
Correct reaction	17 (47%)	1 (3%)	Correct reaction	40 (22%)	39 (22%)

Table 4: Student success as it relates to writing a chemical reaction as part of their problem strategy on Question 3 following instruction.

Given the apparent importance of identifying the correct equilibrium expression for Questions 2 and 3, attention was given to investigating this specific essential skill. Overall, a higher percentage of Analytical Chemistry students (84%) included a chemical reaction of some kind when answering Question 3 than did General Chemistry students (64%). While it is possible that students could omit this step if it is not part of their problem strategy, in only 9/72 cases (13%) were students successful without writing the reaction. This suggests that an omission of this step was not because it was trivial, but rather because these students did not conceptualize the problem and lacked a problem strategy. About 20% of the students in both classes who included an incorrect reaction were successful. The most significant difference is found among students that included the correct reaction. In the upper-level course, in 17/18 cases (94%), students including the correct reaction were successful, whereas in General Chemistry, the value is only 40/79 cases (51%). Overall, writing the correct reaction equation appears to be necessary but not sufficient. For this complex algorithm, upper-level students are very likely to succeed if they can write the correct reaction, but novice students may still falter on a subsequent step.

Key findings for Questions 2 and 3.

- On pre-tests for General Chemistry students, unsuccessful students often did not understand the K_b convention.
- On pre-tests for Analytical Chemistry students, a common flawed problem strategy that included several essential skills was used by multiple students. It is not clear why this incorrect framework is recalled by upper-level students.
- Successful students on the post-test used the same problem strategy and employed the same memorized algorithm.
- Unsuccessful students on the post-test used many essential skills correctly, but also incorrectly applied heuristics, such as the Henderson-Hasselbalch equation, and lacked an appropriate strategy. Many of these errors begin with misidentifying the appropriate equilibrium reaction.
- An important feature of a successful problem strategy is writing the equilibrium reaction. Student errors are not generally mathematical, but rather involve problem conceptualization. This observation has instructional implications.

Question 4: Amount of Solution to Neutralize an Acid or Base

Question 4 is different than Questions 1-3 because it does not involve a pH calculation. Instead, it involves an acid-base neutralization reaction and calculating the volume of solution necessary to neutralize a strong acid or a strong base. This is a common stand-alone topic, and also an initial step in more advanced titration scenarios like Question 5.

In the working model of chemistry problem-solving for Question 4, *problem conceptualization* involves identifying this as an acid-base reaction for two solutions. *Essential skills* include identifying a strong acid and a strong base given their chemical formula, understanding and using solution information such as concentration and volume, and understanding the manner in which a strong electrolyte dissociates. Unlike other questions in this study, there are two plausible *problem strategies* students could employ. One of these strategies is based on a *heuristic* that uses the equation $M_1V_1=M_2V_2$, and the other is a more explicit calculation of the moles of the reactants. Both the Acid and Base Versions include one electrolyte that dissociates in a 1:1 ratio and another that dissociates in a 1:2 ratio, and this raises possibility of a *bottom-up mechanism* similar to the students utilized on the Base Version of Question 1.

Compared to the other questions, the overall results for Question 4 have several unusual features. As shown in Figure 4, on pre-tests the General Chemistry students are far more successful here than on Questions 2, 3, or 5. This is consistent with their having more extensive prior knowledge of this topic, as described below (Figure 14). The pre-test scores for the Analytical Chemistry students were also highest for this question, but their subsequent gain following instruction was modest (Table 3).

On the pre-test, many General Chemistry students are successful, and this should not be too surprising. This type of neutralization question and the identical topic, including all of the essential skills, are found in first semester General Chemistry. As one student noted "This reminds me of a Chemistry 1210 question. Need to use some kind of dimensional analysis. Possibly need balanced chemical eqn?" It should be noted that this student did *not* answer the question; they recognized the question format but did not recall the problem strategy. Nearly all General Chemistry textbooks include the topic of solution stoichiometry in the first semester and then return to it in the second semester.[6] The topic is also included in Analytical Chemistry textbooks.[10] There is not, however, a consensus as to the appropriate problem strategy, which is unusual for standard algorithmic questions.

In all chemistry stoichiometry problems, the reactants combine with each other based on the *amount* of the reactants that are present, often expressed as mole amounts, consistent with the coefficients in the balanced chemical equation. For many stoichiometry questions, the problem strategy begins by 1) writing a balanced equation (if one is not provided), and 2) calculating the number of moles. Calculating the number of moles may involve different tasks depending on the type of problem, such as the use of the periodic table if mass values are given, or the application of the Ideal Gas law when investigating gas stoichiometry. For solution stoichiometry problems, the number of moles is calculated based on the concentration of the solution and its volume. After using the balanced chemical equation to account for the manner in which the reactants react and their amounts, many questions require another conversion to report quantities like grams of product formed, or the pressure of the gas produced. A summary of this problem strategy that explicitly determines mole amounts is featured in Figure 14. Notice how this approach includes three calculations.

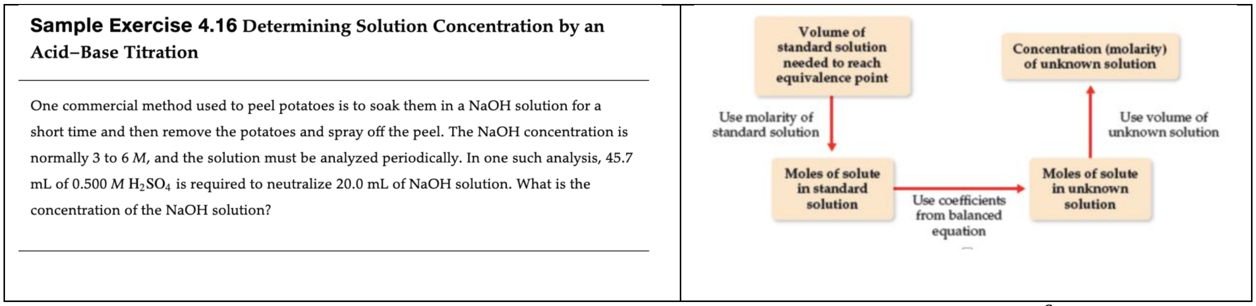


Figure 14: Sample exercise and problem strategy from Brown, LeMay, Bursten[6] textbook. The strategy includes explicit determination of moles. The authors' worked solution is shown in Appendix B.

Some authors suggest a heuristic as a short-cut when answering solution stoichiometry problems. The formula "$M_1V_1=M_2V_2$" where M = concentration, V= volume, and the subscripts denote different solutions, is a quicker way to answer this type of question when three of the four variables are provided. General Chemistry textbooks include this formula, but most use it to describe calculations for diluting solutions, not for reaching the equivalence point in a neutralization reaction. However, some Analytical textbooks do describe this approach as the appropriate problem strategy for neutralization reactions (Figure 15).[10] Notice how this approach includes only one, well-defined calculation with one unknown.

How do these two problem strategies (explicitly calculating moles vs. the $M_1V_1=M_2V_2$ heuristic) compare with each other? Explicitly calculating moles includes more steps and is more complex, and this may lead to greater cognitive load and more opportunities to commit an error. Depending on how it is executed, it may also require additional mathematical essential skills, such as proportional reasoning. The $M_1V_1=M_2V_2$ heuristic is a useful short-cut, but like other heuristics the user must be aware of its limitations. In particular, as written, the equation is only applicable when the ratio of the coefficients for reactants is 1:1. If this is not true, the equation can still be utilized but additional steps are required. This assumption is valid for the example shown in Figure 15. It is not valid for the example shown in Figure 14, and it is not valid for Question 4.

TITRATING STRONG ACIDS AND STRONG BASES

For our first titration curve, let's consider the titration of 50.0 mL of 0.100 M HCl using a titrant of 0.200 M NaOH. When a strong base and a strong acid react the only reaction of importance is

$$H_3O^+(aq) + OH^-(aq) \longrightarrow 2H_2O(l) \qquad 9.1$$

The first task is to calculate the volume of NaOH needed to reach the equivalence point, V_{eq}. At the equivalence point we know from reaction 9.1 that

$$\text{moles HCl} = \text{moles NaOH}$$

$$M_a \times V_a = M_b \times V_b$$

where the subscript '*a*' indicates the acid, HCl, and the subscript '*b*' indicates the base, NaOH. The volume of NaOH needed to reach the equivalence point is

$$V_{eq} = V_b = \frac{M_a V_a}{M_b} = \frac{(0.100\text{ M})(50.0\text{ mL})}{(0.200\text{ M})} = 25.0\text{ mL}$$

Before the equivalence point, HCl is present in excess and the pH is determined by the concentration of unreacted HCl. At the start of the titration the solution is 0.100 M in HCl, which, because HCl is a strong acid, means the pH is

Figure 15: Problem strategy from the Harvey[10] Analytical Chemistry textbook using the $M_1V_1=M_2V_2$ heuristic to calculate the volume needed to reach the equivalence points.

The Acid and Base Versions were written to be equivalent, with both including a 1:2 ratio of coefficients in the balanced reaction (which was not provided). Student writing revealed a potential threat to the validity of the Acid Version, which included sulfuric acid, H_2SO_4, as a reactant. Sulfuric acid is a strong electrolyte with respect to donating the first proton, but HSO_4^- is a weak acid. This does not actually affect the calculation, and it does not affect the volume necessary to reach the equivalence point. If students raised this point in their shown work, they were given credit for correctly answering the question (Figure 16). This is something to keep in mind if this question is used in a testing situation that does not include an analysis of student writing.

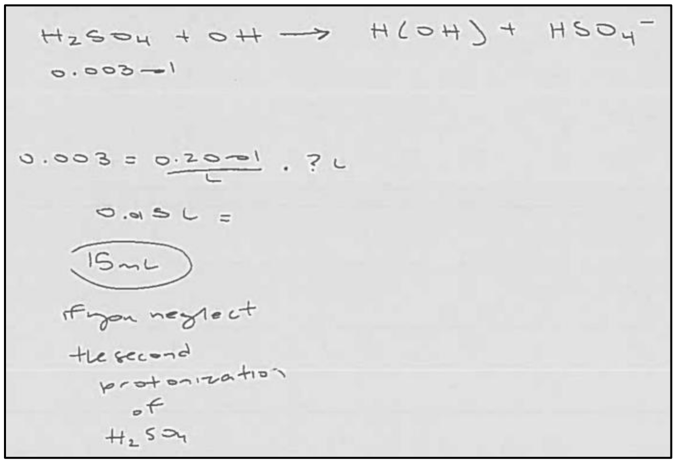
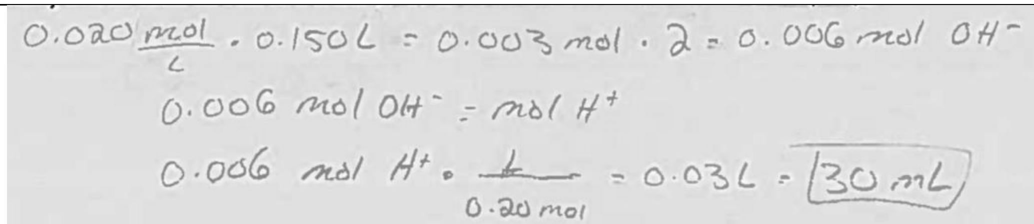
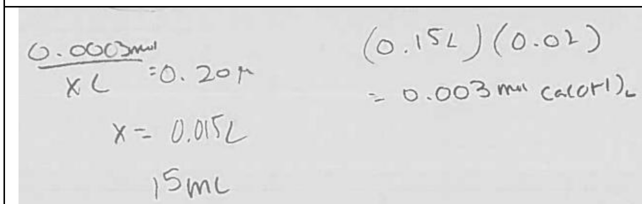


Figure 16: Shown work for Question 4 in which HSO4$^-$ is identified as a weak acid.

Analysis of the post-test results indicates that both problem strategies were prevalent in both classes. This is noteworthy because the M_1V_1 heuristic was not included in the instructional period relating to solving neutralization problems, and yet many students utilize this problem strategy. There are cases in which each strategy leads to success, and cases in which each strategy leads to failure.

Examples in which students explicitly calculate the number of moles are shown in Figure 17. This approach includes several steps, and students generally do not bother to include a balanced equation. This can lead to errors when accounting for the dissociation. Also, some students determine the number of moles involved in the reaction but have difficulty calculating the resulting volume.





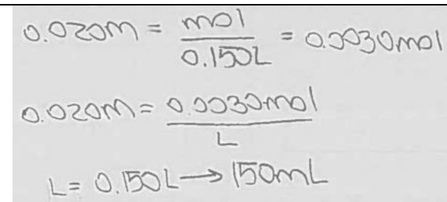
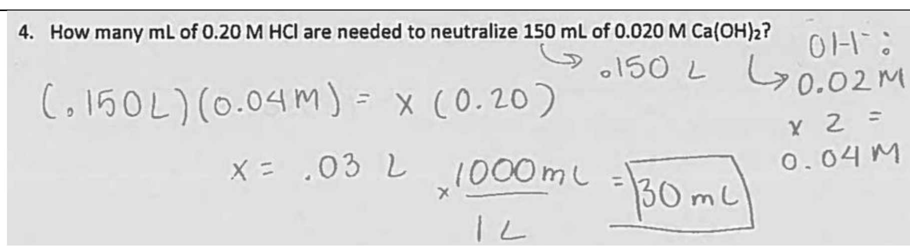
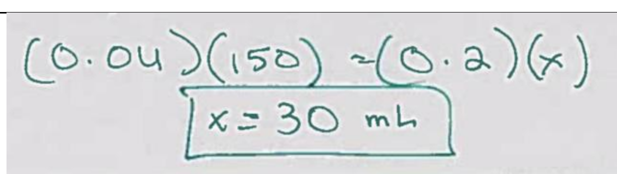


Figure 17: Shown work Question 4 and explicitly calculating number of moles: Correct application of the strategy (top), failure to account for dissociation (left), other error (right).

Examples in which students apply $M_1V_1=M_2V_2$ are shown in Figure 18. Some students draw attention to the fact that the balanced equation does not result in a 1:1 relationship for the reactants. In most cases, however, successful students do not explicitly state this in their problem-solving; they account for it in their written equation, but do not explain their reasoning. Finally, there are examples in which students use the provided numbers but fail to account for the manner of dissociation.





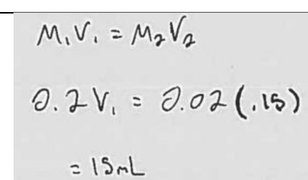


Figure 18: Shown work Question 4 and applying $M_1V_1=M_2V_2$: Correct application of the strategy and identifying manner of dissociation (top), correct application, correct dissociation inferred (left); failure to account for dissociation (right).

On the post-tests Analytical Chemistry students were more successful than the General Chemistry students using either approach (Table 5). In addition, both Analytical and General Chemistry students that explicitly calculated the number of moles were more successful than those using the $M_1V_1=M_2V_2$ strategy.

Analytical Chemistry			General Chemistry		
	Mole Analysis	M_1V_1		Mole Analysis	M_1V_1
Successful	12 (33%)	9 (25%)	Successful	49 (31%)	19 (12%)
Unsuccessful	4 (11%)	11 (31%)	Unsuccessful	47 (29%)	45 (28%)
% Successful	75%	45%	% Successful	50%	30%

Table 5: The success of different problem strategies on Question 4 after instruction.

General Chemistry students who used the Mole Analysis strategy were more likely to make extraneous errors (19%) than those who used the M_1V_1 equation (9%). The Mole Analysis method is longer, increasing the cognitive load on the students, and yielding the opportunity for more extraneous mistakes. It was found that 19% of students who used the Mole Analysis strategy made an extraneous error, compared to only 9% of students who used the M_1V_1 method. However, students who used the M_1V_1 approach were nearly three times as likely to fail to account for the dissociation of the strong electrolyte (61%) than those who used the Mole Analysis approach (22%), leading to an incorrect answer. Students using the M_1V_1 approach needed to intentionally account for the 2:1 dissociation ratio in order to be successful, and 61% of students failed to do this. It is clear that students are overall more successful when they utilize the Mole Analysis method.

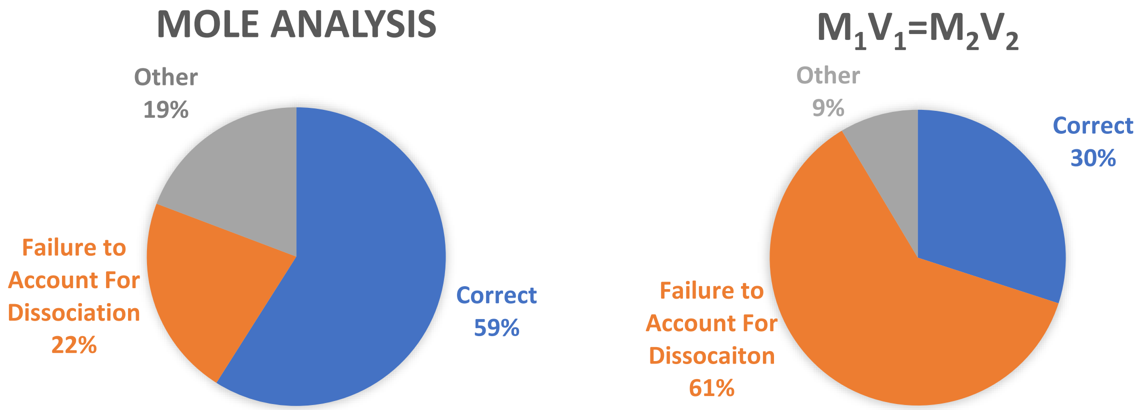


Figure 19: The outcomes of different strategies utilized by General Chemistry students on Question 4 after instruction. Students who did not account for the 1:2 ratio of dissociation for a strong electrolyte were classified as Failure to Account for Dissociation. Other errors included calculation errors and no response.

Given the stark difference in performance for these two problem strategies, it is appropriate to keep in mind what was being compared. For several reasons, this study is one in which the $M_1V_1=M_2V_2$ has particular vulnerabilities. This heuristic was not included in the instructional period, and so students may not be aware of its limitations. Indeed, the central shortcoming of this approach (when the ratio of the coefficients for the reactants is not one) is precisely where many students went wrong on this question. Finally, a balanced equation was not provided in the question, but concentration and volume information were, leading students to quickly adopt a bottom-up mechanism that seemed appropriate.

Key Findings for Question 4

- Two problem strategies, explicitly determining number of moles and the $M_1V_1=M_2V_2$ heuristic, are found in chemistry textbooks.
- The $M_1V_1=M_2V_2$ strategy is prevalent on post-tests, even when it is not included during the instruction period.

- The $M_1V_1=M_2V_2$ strategy is prone to errors in accounting for dissociation as students apply this heuristic without accounting for its limitations.
- The Mole Analysis strategy leads to greater success, but it includes more essential skills that must be mastered and is susceptible to a greater diversity of errors.

Question 5: Titration with Excess Strong Electrolyte

Scenarios involving titrations are found in General and Analytical Chemistry. They are algorithmic exercises in which the problem-solver must initially *conceptualize* the problem and identify whether it involves two strong electrolytes, or one strong electrolyte and one weak electrolyte. This includes the *essential skills* of being able to identify strong and weak acids and bases given their formula. The problem strategy for a titration problem involves determining what region of the titration is applicable and then utilizing the correct algorithm. In a sense, there is a back and forth between problem conceptualization and problem strategy for a titration question in which the solver conceptualizes the problem, applies a problem strategy that then leads to conceptualization of another problem and finally apply another problem strategy to reach the problem solution. In the case of Question 5 this entails 1) identifying a reaction between a strong electrolyte and weak electrolyte, 2) determining that the strong electrolyte is in excess, and 3) calculating the pH after accounting for the stoichiometry of the neutralization reaction and the increased volume. Another challenge to the problem solver is the fact that heuristics mentioned thus far, such as the Henderson-Hasselbalch equation, are applicable for some regions of a titration curve but not others. In this situation, a bottom-up mechanism in which a heuristic is misapplied is quite possible.

Given the complex, two-step nature of titration problems, it is unsurprising that both the pre-test and post-test scores are low for both classes. What is noteworthy is that, following instruction, the Analytical Chemistry students scored *lower* than the General Chemistry students. This is the only question and testing stage in which such an occurrence is found. To understand this phenomenon the qualitative response data must be analyzed.

Of all of the questions on the instrument, Question 5 had the greatest variety of strategies utilized by students. Four problem-solving strategies were prevalent in both courses: a Before-Change-After (BCA) table to account for the reaction stoichiometry, an ICE table to analyze equilibrium amounts, the Henderson-Hasselbalch equation to account for buffer conditions, and a Mole Analysis. General Chemistry students were far more likely to use a BCA table, and Analytical Chemistry students more likely to use the strategies that account for equilibrium conditions, which are ICE tables and the Henderson-Hasselbalch equation (Figure 20). Each of these strategies are additional information that the students encounter during instruction. Not all of these strategies are applicable to the problem at hand, yet students continued to attempt to use them while solving this question. The diversity of problem-solving strategies suggests that students don't have a clear problem conceptualization and problem strategy. Part of the reason for this may be due to the layering of acid-base concepts in instruction. When these layers, such as ionic theory and equilibrium theory, are not clearly defined and integrated, learning problems can arise.[8]

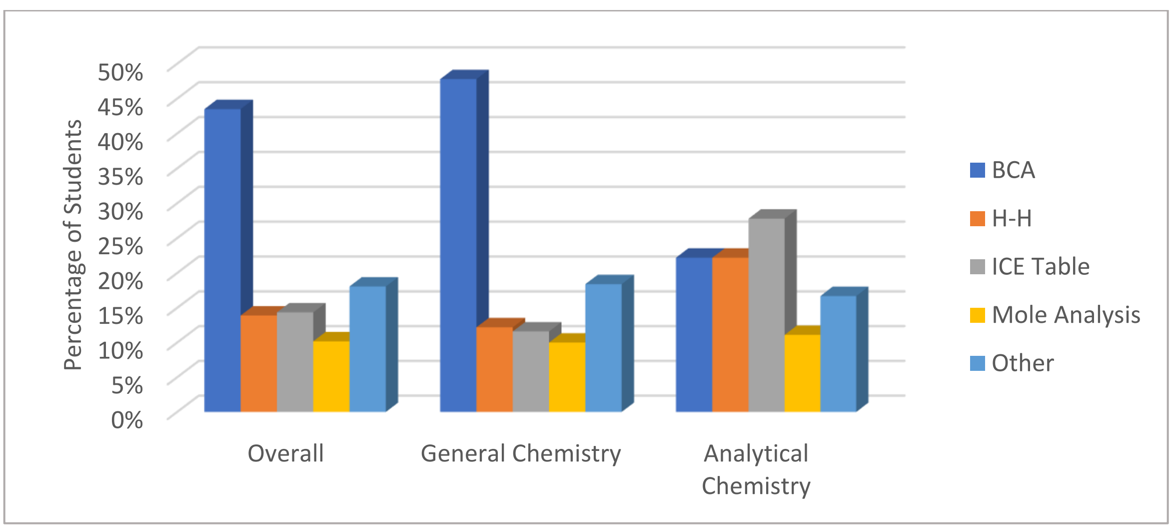


Figure 20: The strategies used by students on Question 5 after instruction. H-H refers to students who used the Henderson-Hasselbalch equation.

Although titration scenarios may lead to the use of equilibrium heuristics like the Henderson-Hasselbalch equation, the scenario described in Question 5 is not one of them. In other words, when the Analytical Chemistry students use either an ICE table or the Henderson-Hasselbalch equation, they have not succeeded at problem conceptualization and are misapplying a heuristic. The thought process leading to use of the Henderson-Hasselbalch is easy to infer; in Figure 21, the student calculated mole amounts for an acid and a base and either recognized these as variables in the Henderson-Hasselbalch equation, or initially conceptualized the problem as suitable for the Henderson-Hasselbalch equation. Similar to previous questions in this study, many students in both courses attempted to use the Henderson-Hasselbalch equation, despite this being an inappropriate application of the equation. This question asks about a solution with an excess amount of strong electrolyte, while the Henderson-Hasselbalch equation is a strategy that is used to solve buffer problems. This is another example of students being unable to correctly identify the concept in the problem and therefore resorting to inappropriately utilizing an algorithmic, bottom-up strategy.

The use of an ICE table as a problem strategy was not anticipated, yet it was found among several students. In these cases, the student began by first determining the equilibrium concentration of the weak electrolyte, and then used this amount in a stoichiometric reaction with the strong electrolyte. This is not a standard algorithmic approach, and the student is not understanding that the equilibrium conditions do not apply when a strong acid or strong base is in excess. However, given that the Analytical Chemistry students are frequently working with equilibrium calculations, they become very proficient with ICE tables, so it makes sense that their first impulse may be to account for the equilibrium in Question 5 even when it is not appropriate. This is partially why the upper-level student struggle with Question 5 in ways their General Chemistry counterparts do not.

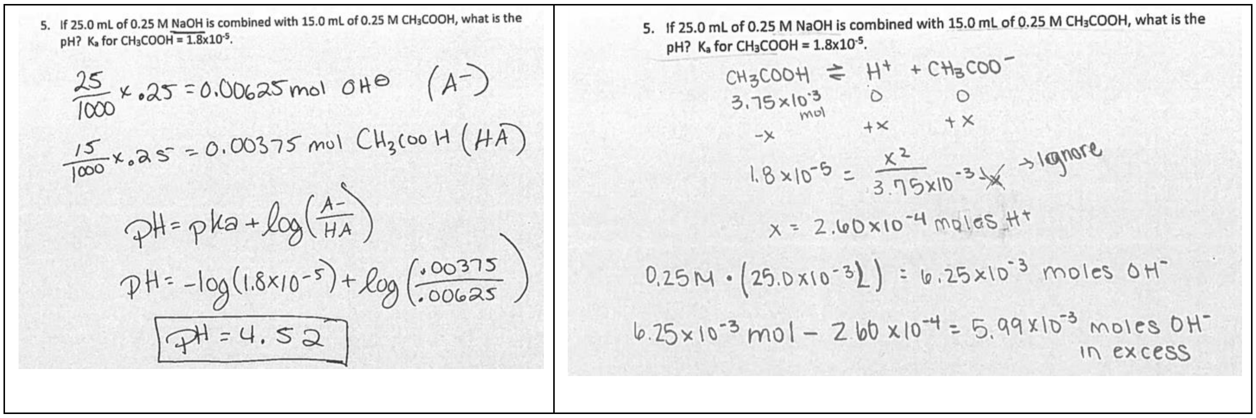


Figure 21: Analytical Chemistry students use of the Henderson-Hasselbalch equation (left) or ICE tables (right) when answering Question 5.

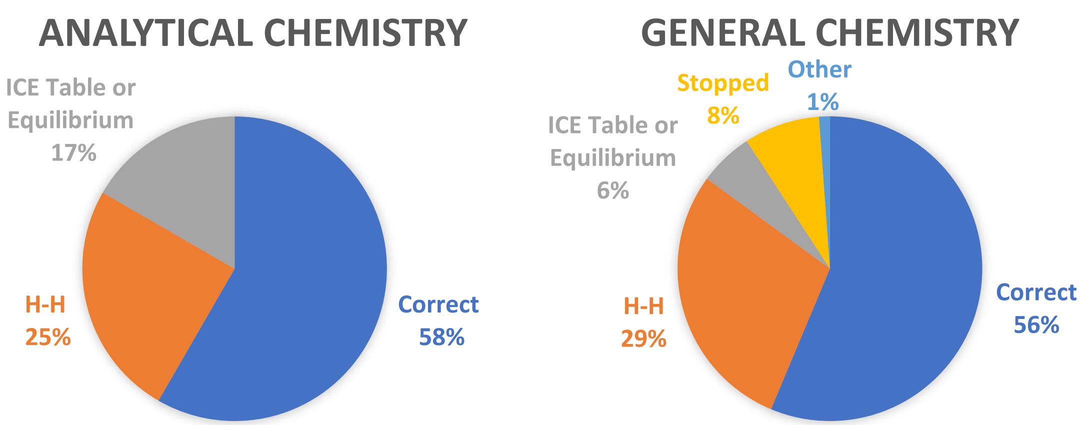


Figure 22: Student strategy following the successful completion of a BCA table on Question 5 after instruction. H-H refers to using the Henderson-Hasselbalch equation. Other errors include mathmatical errors or no response.

Many students in both courses were able to complete a BCA table, which is the beginning of the correct problem-solving strategy; however, of the students that were able to complete this step, only a little over half went on to successfully solve the problem in both courses. The Analytical Chemistry students were more likely to attempt to use an ICE Table or analyze an equilibrium following a BCA table than the General Chemistry students, demonstrating their tendency to attempt to apply more advanced ideas. About a quarter of these students resorted to using the Henderson-Hasselbalch equation following a BCA table, again demonstrating an inability to recognize that there is an excess amount of a strong electrolyte and that the solution is not a buffer.

Key Findings

- Titrations scenarios, like Question 5, are particularly difficult because they require more than one problem conceptualization stage.
- Some titration scenarios lead to problem strategies that account for the resulting equilibrium, such as use of the Henderson-Hasselbalch equation for a buffer. This is a compelling heuristic that is misapplied when answering Question 5.
- Beginning Question 5 by first calculating the equilibrium concentration of the weak electrolyte was an error found among upper-level students, but not General Chemistry students. This explains, in part, why Analytical Chemistry students underperformed on this question when compared to General Chemistry students.

Conclusion

When confronted with quantitative problems in their General and Analytical Chemistry courses, students often struggle to be successful. Students have difficulty solving acid-base equilibria problems that incorporate students' conceptual knowledge of the topic with their problem-solving skills. There is a clear distinction between the methods used by experts and the methods used by novices when solving quantitative problems. For the questions used in this study, both expert and novice students used algorithms and included various relevant essential skills in their problem-solving. However, novices struggled to conceptualize the problem, recall the appropriate problem-solving strategy, and use the appropriate heuristics.

There were very strong normalized gains among both General chemistry and Analytical Chemistry students for the simpler questions following instruction. However, as the questions increased in difficulty, many students struggled to identify the question's concept and therefore could not complete the appropriate problem-solving strategy. The analysis of student work suggests that when students are unable to recognize a concept, they may utilize bottom-up reasoning methods and inappropriate algorithmic heuristics. For example, many students used the Henderson-Hasselbalch equation for problems that did not involve buffers. For Question 4, students frequently opted to use the $M_1V_1 = M_2V_2$ equation instead of explicitly calculating the moles of the species present in the solution. Although this heuristic could be used successfully by intentionally accounting for the dissociation of a diprotic or dibasic electrolyte, many students failed to account for this feature when using this heuristic, leading to an incorrect response. For the Analytical Chemistry students, another common error was including advanced ideas that were not applicable for the particular question. The prior knowledge that the Analytical students have extend beyond the scope of the questions in the instrument, but many Analytical students still attempted to apply these ideas to the problems at hand, leading to unsuccessful results. This problem-solving pattern became apparent in Question 5 when students would attempt to apply an ICE table or equilibrium analysis when it was not applicable.

This study also highlights the importance of qualitatively analyzing the students problem-solving process. Utilizing an open-ended instrument on such a large scale allowed for an in-depth analysis of student responses that a quantitative instrument would not have. Qualitatively coding for student responses lead to the detection of certain elements and patterns within the student problem-solving process. Although previous qualitative studies about student performance on acid-base equilibria problems have been conducted, this particular study is one of the first to be conducted on this scale, which is novel in both the participant sample size and the pseudo-longitudinal timeline. Over 400 student tests were qualitatively coded, allowing for an in-depth view of the student problem-solving process. Additionally, this allowed for the comparison of the problem-solving process of novice General Chemistry students with that of upper-level Analytical Chemistry students. With this format, student prior knowledge, essential skills, and use of heuristics were able to be identified and mapped across groups of students. Instead of attributing student failure to a general lack of understanding, the exact mistakes could be identified within a student's response. By pinpointing the point of breakdown in student understanding, instructors are informed about where to focus their curriculum in order to promote student success.

Finally, this research also has various implications for instructors and educators. There should be a focus on the development of students' abilities to recognize a concept and apply the correct strategy, as this data shows that students struggle with concept recognition, impeding their ability to apply the correct problem-solving strategy. This data informs instructors to turn their attention to developing several aspects of students' problem-solving abilities: their problem conceptualization, essential skills, and execution of problem strategy. As seen in this study, successful students are able to recognize the concept in a question and draw upon their prior knowledge, additional knowledge, and essential skills to correctly execute the appropriate problem-solving strategy. Instructors can help students achieve this level of success by placing an emphasis on both concept recognition, essential skills, and problem-solving strategy during the instructional period. Clarifying which essential skills should be used for which problem should also be stressed during instruction. As seen in the data, many students inappropriately applied heuristics that they learned during the instructional period. For example, emphasizing that the Henderson-Hasselbalch equation is only a useful heuristic for buffer problems could help reduce the number of students that attempt to generalize this equation for any acid-base equilibria problem. Overall, this study highlights that each of the problem-solving aspects analyzed in this study must be present in instruction for students to be set up for success.

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Appendix A: Worked Solutions

Question 1:

Acid Version

The first question on the assessment asks students to determine the pH of a strong acid or strong base. To solve the Acid Version of Question 1, the student must first identify that the acid, HI, is a strong acid. As a strong acid, it will completely dissociate in solution; therefore $[H^+]$ will be equal to [HI]. They then must recall the equation that expresses pH in terms of $[H^+]$:

$$pH = -\log([H^+]) \tag{Equ. 1}$$

The student can then use this equation and the $[H^+]$ to determine pH.

Base Version

Solving the Base Version of Question 1 involves a similar process with a few additional steps. As with the Acid Version, the student must recognize that $Sr(OH)_2$ is a strong base and will completely dissociate in solution. However, the student also needs to identify that for every molecule of $Sr(OH)_2$, two molecules of OH^- are produced so that the $[OH^-]$ is twice that of $[Sr(OH)_2]$. The student must then recall the equation that expresses pOH in terms of $[OH^-]$:

$$pOH = -\log([OH^-]) \tag{Equ. 2}$$

The student can use this equation to determine pOH. From there, the student must relate pOH to pH using the following equation:

$$pH + pOH = 14.00 \tag{Equ. 3}$$

Using the above equation, the student can solve for pH.

Question 2:

The second question on the assessment asks students to determine the pH of a weak acid or weak base. By definition, weak acids and bases only partially ionize in solution. The degree to which a weak acid or weak base will ionize is given by its K_a or K_b value, respectively. The equilibrium expression for a weak acid, HA, can be expressed as:

$$K_a = ([H^+][A^-])/[HA]$$

H^+ is synonymous with H_3O^+.The equilibrium expression for a weak base, B, can be expressed as:

$$K_b = ([BH^+][OH^-])/[B]$$

Acid Version

The student is asked to find the pH of a 2.0 M solution of HF. The student must identify HF as a weak acid, and the write the ionization equilibrium reaction for HF:

$$HF_{(aq)} + H_2O_{(l)} \leftrightarrow H^+_{(aq)} + F^-_{(aq)}$$

From the equilibrium, the student can write the equilibrium expression that relates K_a to the concentration of the species involved in the equilibrium:

$$K_a = ([H^+][F^-])/[HF]$$

The student can then construct an ICE (Initial concentration, Change in concentration, and Equilibrium concentration) table where they can quantify the extent of dissociation as *x* moles.

	$HF_{(aq)}$ +	$H_2O_{(l)}$ $\leftrightarrow$	$H^+_{(aq)}$ +	$F^-_{(aq)}$
Initial Concentration (M)	2.0	--	0	0
Change in Concentration (M)	- x	--	+ x	+ x
Equilibrium Concentration (M)	2.0 - x	--	x	x

The student can now plug the equilibrium concentration values of the three species along with the value of K_a back into the equilibrium expression to solve for *x*, which is also equal to the equilibrium concentration of $[H^+]$:

$$6.6x10^{-4} = (x \bullet x)/(2.0 - x)$$

or

$$6.6x10^{-4} = (x^2)/(2.0 - x)$$

To simplify the equation, it can be assumed that the value of *x* is negligible compared to 2.0, so the quantity of (2.0 - x) can be assumed to be 2.0, yielding:

$$6.6x10^{-4} = (x^2)/(2.0)$$

The equilibrium concentration of $[H^+]$ can then be determined by solving for *x*. To ensure that the assumption was valid, the student should check to see that the value of *x* is less than 5% of the original value for [HF], which it is. Once the student has obtained a value for $[H^+]$, the student can then solve for pH using Equ. 1.

Base Version

The student is asked to find the pH of a 2.0 M solution of CH_3NH_2. The student must identify CH_3NH_2 as a weak base, and the write the ionization equilibrium reaction for CH_3NH_2:

$$CH_3NH_{2\,(aq)} + H_2O_{(l)} \leftrightarrow CH_3NH_3^+{}_{(aq)} + OH^-_{(aq)}$$

From the equilibrium, the student can write the equilibrium expression that relates K_b to the concentration of the species involved in the equilibrium:

$$K_b = ([CH_3NH_3^+][OH^-])/[CH_3NH_2]$$

The student can then construct an ICE table where they can quantify the extent of dissociation as *x* moles.

	$CH_3NH_{2\,(aq)}$ +	$H_2O_{(l)}$ $\leftrightarrow$	$CH_3NH_3^+{}_{(aq)}$ +	$OH^-{}_{(aq)}$
Initial Concentration (M)	2.0	--	0	0
Change in Concentration (M)	- x	--	+ x	+ x
Equilibrium Concentration (M)	2.0 - x	--	x	x

The student can now plug the equilibrium concentration values of the three species along with the value of K_b back into the equilibrium expression to solve for *x*, which is also equal to the equilibrium concentration of $[OH^-]$:

$$4.38x10^{-4} = (x \bullet x)/(2.0 - x)$$

or

$$4.38x10^{-4} = (x^2)/(2.0 - x)$$

To simplify the equation, it can be assumed that the value of *x* is negligible compared to 2.0, so the quantity of (2.0 - x) can be assumed to be 2.0, yielding:

$$4.38x10^{-4} = (x^2)/(2.0)$$

The equilibrium concentration of $[OH^-]$ can then be determined by solving for *x*. To ensure that the assumption was valid, the student should check to see that the value of *x* is less than 5% of the original value for $[CH_3NH_2]$, which it is. Once the student has obtained a value for $[OH^-]$, the student can then solve for pOH using Equ. 2. The student can then convert from pOH to pH using Equ. 3. The problem-solving process for the Base Version mirrors that of the Acid Version, with the additional step of converting from pOH to pH.

Question 3:

The third question in the assessment asks students to determine the pH of a salt solution. The student will need to identify the anion and cation present in the salt and then determine whether or not the anion or cation will react with water to produce H^+ or OH^-.

Acid Version

The student is asked to determine the pH of a 0.25 M solution of NH_4Cl. First the student must identify NH_4Cl as a salt where Cl^- is the anion and NH_4^+ is the cation. Since Cl^- is the conjugate base of a strong acid, HCl, the student must identify that the Cl^- in the solution will not react significantly with H_2O and therefore will not affect pH. On the other hand, the student must identify that the NH_4^+ in the solution is the conjugate acid of a weak base and therefore will react with H_2O to produce H^+ which will in turn affect the pH of the solution. The student should start by writing the reaction between NH_4^+ and H_2O:

$$NH_4^+{}_{(aq)} + H_2O_{(l)} \leftrightarrow H^+{}_{(aq)} + NH_{3\,(aq)}$$

From the equilibrium, the student can write the equilibrium expression that relates K_a to the concentration of the species involved in the equilibrium:

$$K_a = ([H^+][NH_3])/[NH_4^+]$$

In this problem, the student is not given the K_a of NH_4^+, but is instead given the K_b of NH_3. Therefore the student will have to solve for K_a using the following equation:

$$K_a \bullet K_b = K_w = 1.0x10^{-14} \qquad \text{Equ. 4}$$

By substituting in the given K_b value of $1.8x10^{-5}$, the student can solve for K_a to obtain a value of $5.6x10^{-10}$. The student can then construct an ICE table where they can quantify the extent of dissociation as *x* moles.

	$NH_4^+{}_{(aq)}$ +	$H_2O_{(l)}$ $\leftrightarrow$	$H^+{}_{(aq)}$ +	$NH_{3\,(aq)}$
Initial Concentration (M)	0.25	--	0	0
Change in Concentration (M)	- x	--	+ x	+ x
Equilibrium Concentration (M)	0.25 - x	--	x	x

The student can now plug the equilibrium concentration values of the three species along with the value of K_a back into the equilibrium expression to solve for *x*, which is also equal to the equilibrium concentration of $[H^+]$:

$$5.6x10^{-10} = (x \bullet x)/(0.25 - x)$$

or

$$5.6x10^{-10} = (x^2)/(0.25 - x)$$

To simplify the equation, it can be assumed that the value of *x* is negligible compared to 0.25, so the quantity of (0.25 - x) can be assumed to be 0.25, yielding:

$$5.6x10^{-10} = (x^2)/(0.25)$$

The equilibrium concentration of $[H^+]$ can then be determined by solving for *x*. To ensure that the assumption was valid, the student should check to see that the value of *x* is less than 5% of the original value for $[NH_4^+]$. Once the student has obtained a value for $[H^+]$, the student can then solve for pH using Equ. 1.

Base Version

The student is asked to determine the pH of a 0.25 M solution of NaF. First the student must identify NaF as a salt where Na^+ is the cation and F^- is the anion. Since Na^+ is the conjugate acid of a strong base, NaOH, the student must identify that the Na^+ in the solution will not react significantly with H_2O and therefore will not affect pH. On the other hand, the student must identify that the F^- in the solution is the conjugate base of a weak acid and therefore will react with H_2O to produce OH^- which will in turn affect the pH of the solution. The student should start by writing the reaction between F^- and H_2O:

$$F^-{}_{(aq)} + H_2O_{(l)} \leftrightarrow HF_{(aq)} + OH^-{}_{(aq)}$$

From the equilibrium, the student can write the equilibrium expression that relates K_b to the concentration of the species involved in the equilibrium:

$$K_b = ([HF][OH^-])/[F^-]$$

In this problem, the student is not given the K_b of F^-, but is instead given the K_a of HF. Therefore the student will have to solve for K_b using Equ. 4. By substituting in the given K_a value of $6.6x10^{-4}$, the student can solve for K_b to obtain a value of $1.5x10^{-11}$. The student can then construct an ICE table where they can quantify the extent of dissociation as *x* moles.

	$F^-{}_{(aq)}$ +	$H_2O_{(l)}$ $\leftrightarrow$	$HF_{(aq)}$ +	$OH^-{}_{(aq)}$
Initial Concentration (M)	0.25	--	0	0
Change in Concentration (M)	- x	--	+ x	+ x
Equilibrium Concentration (M)	0.25 - x	--	x	x

The student can now plug the equilibrium concentration values of the three species along with the value of K_b back into the equilibrium expression to solve for *x*, which is also equal to the equilibrium concentration of $[OH^-]$:

$$1.5x10^{-11} = (x \bullet x)/(0.25 - x)$$

or

$$1.5x10^{-11} = (x^2)/(0.25 - x)$$

To simplify the equation, it can be assumed that the value of x is negligible compared to 0.25, so the quantity of (0.25 - x) can be assumed to be 0.25, yielding:

$$1.5x10^{-11} = (x^2)/(0.25)$$

The equilibrium concentration of $[OH^-]$ can then be determined by solving for x. To ensure that the assumption was valid, the student should check to see that the value of x is less than 5% of the original value for $[F^-]$. Once the student has obtained a value for $[OH^-]$, the student can then solve for pOH using Equ. 2, and then solve for pH using Equ. 3. Again, this question mirrors the Acid Version with the addition of converting from pOH to pH.

Question 4:

This question asks the student to determine the amount of a solution needed to neutralize a given solution. To solve this question, the student needs to understand that when a solution is neutralized, $[H^+]$ is equal to $[OH^-]$.

Acid Version

The student must first determine the amount of H^+ that is present in the 0.020M solution of H_2SO_4. This can be done using stoichiometric conversions:

150 mL	1 L	0.020 mol H_2SO_4	2 mol H^+	= 0.0060 mol H^+
	1,000 mL	1 L	1 mol H_2SO_4	

An important step in this process is taking into account the dissociation of the strong acid H_2SO_4, yielding two moles of H^+ per one mole of H_2SO_4.

The student must then be able to identify that, to be neutralized, the amount of moles of H^+ must be equal to the amount of moles of OH^-. Therefore, the amount of OH^- needed to neutralize this solution is 0.0060 moles. Since the molarity of the KOH solution being used to neutralize the H_2SO_4 solution is given, it can be used to convert from moles of OH^- to the volume of the KOH solution needed:

0.0060 mol OH^-	1 mol KOH	1 L KOH	1,000 mL KOH	= 30 mL KOH
	1 mol OH^-	0.20 mol KOH	1 L KOH	

Base Version

The student must first determine the amount of OH^- that is present in the 0.020M solution of $Ca(OH)_2$. This can be done using stoichiometric conversions:

150 mL	1 L	0.020 mol $Ca(OH)_2$	2 mol OH^-	= 0.0060 mol OH^-
	1,000 mL	1 L	1 mol $Ca(OH)_2$	

An important step in this process is taking into account the dissociation of the strong acid $Ca(OH)_2$, yielding two moles of OH^- per one mole of $Ca(OH)_2$.

The student must then be able to identify that, to be neutralized, the amount of moles of H^+ must be equal to the amount of moles of OH^-. Therefore, the amount of H^+ needed to neutralize this solution is 0.0060 moles. Since the molarity of the HCl solution being used to neutralize the $Ca(OH)_2$ solution is given, it can be used to convert from moles of H^+ to the volume of the HCl solution needed:

0.0060 mol H^+	1 mol HCl	1 L HCl	1,000 mL HCl	= 30 mL HCl
	1 mol H^+	0.20 mol HCl	1 L HCl	

The Base Version of this question is almost identical to the Acid Version.

Question 5:

The final question on the assessment asks students to determine the pH of a titration that has an excess amount of a strong electrolyte, so the pH will be dependent on the concentration of the strong acid or base. The student will have to determine the amount of strong acid or base remaining after reacting with the added solution and then use this amount to determine the pH of the solution.

Acid Version

First, the student must determine the moles of acid and base that have been added together. This can be done using stoichiometric conversions:

25.0 mL HNO_3	1 L HNO_3	0.25 mol HNO_3	1 mol H^+	= 0.00625 mol H^+
	1,000 mL HNO_3	1 L HNO_3	1 mol HNO_3	

15.0 mL CH_3NH_2	1 L CH_3NH_2	0.25 mol CH_3NH_2	= 0.00375 mol CH_3NH_2
	1,000 mL CH_3NH_2	1 L CH_3NH_2	

It is important to note that the student must identify HNO_3, as a strong acid so that the student can recognize that for every mol of HNO_3, one mole of H^+ is produced. The student must then write the reaction for the equilibrium between CH_3NH_2 and H^+:

$$CH_3NH_{2\,(aq)} + H^+_{(aq)} \leftarrow\rightarrow CH_3NH_3{}^+_{(aq)} + H_2O_{(l)}$$

From here, the student must determine the amount of H^+ that will remain in solution after it reacts with CH_3NH_2. This can be determined using a BCA (Before reaction, Change, After reaction) table:

	$CH_3NH_{2\,(aq)}$ +	$H^+_{(aq)}$ ←→	$CH_3NH_3^+{}_{(aq)}$ +	$H_2O_{(l)}$
Before Reaction (mols)	0.00375	0.00625	0	--
Change (mols)	- 0.00375	- 0.00375	+ 0.00375	--
After Reaction (mols)	0	0.00250	0.00375	--

The student must recognize that they have found the moles of H^+, not $[H^+]$. To find $[H^+]$, the student will need to divide the moles of H^+ by the new total volume of solution, which can be found by adding the volumes of the two original solutions together. Once the student has calculated $[H^+]$, they can use Equ. 1 to solve for pH.

Base Version

First, the student must determine the moles of acid and base that have been added together. This can be done using stoichiometric conversions:

25.0 mL NaOH	1 L NaOH	0.25 mol NaOH	1 mol OH^-	= 0.00625 mol OH^-
	1,000 mL NaOH	1 L NaOH	1 mol NaOH	

15.0 mL CH_3COOH	1 L CH_3COOH	0.25 mol CH_3COOH	= 0.00375 mol CH_3COOH
	1,000 mL CH_3COOH	1 L CH_3COOH	

It is important to note that the student must identify NaOH, as a strong base so that the student can recognize that for every mol of NaOH, one mole of OH^- is produced. The student must then write the reaction for the equilibrium between CH_3COOH and OH^-:

$$CH_3COOH_{(aq)} + OH^-_{(aq)} \leftrightarrow CH_3COO^-_{(aq)} + H_2O_{(l)}$$

From here, the student must determine the amount of OH^- that will remain in solution after it reacts with CH_3COOH. This can be determined using a BCA table:

	$CH_3COOH_{(aq)}$ +	$OH^-_{(aq)}$ ←→	$CH_3COO^-_{(aq)}$ +	$H_2O_{(l)}$
Before Reaction (mols)	0.00375	0.00625	0	--
Change (mols)	- 0.00375	- 0.00375	+ 0.00375	--
After Reaction (mols)	0	0.00250	0.00375	--

The student must recognize that they have found the moles of OH^-, not $[OH^-]$. To find $[OH^-]$, the student will need to divide the moles of OH^- by the new total volume of solution, which can be found by adding the volumes of the two original solutions together. Once the student has calculated $[OH^-]$, they can use Equ. 2 to solve for pOH and then Equ. 3 to solve for pH. The Base Version mirrors the Acid Version with the additional step of converting from pOH to pH.

Appendix B: Worked Solution for Question 4 from Brown, LeMay, Bursten[5]

Sample Exercise 4.16 Determining Solution Concentration by an Acid–Base Titration

One commercial method used to peel potatoes is to soak them in a NaOH solution for a short time and then remove the potatoes and spray off the peel. The NaOH concentration is normally 3 to 6 *M*, and the solution must be analyzed periodically. In one such analysis, 45.7 mL of 0.500 *M* H_2SO_4 is required to neutralize 20.0 mL of NaOH solution. What is the concentration of the NaOH solution?

Solve

The number of moles of H_2SO_4 is the product of the volume and molarity of this solution:

$$\begin{aligned}\text{Moles } H_2SO_4 &= (45.7\ \cancel{\text{mL soln}})\left(\frac{1\ \cancel{\text{L soln}}}{1000\ \cancel{\text{mL soln}}}\right)\left(\frac{0.500\ \text{mol } H_2SO_4}{\cancel{\text{L soln}}}\right)\\ &= 2.28 \times 10^{-2}\ \text{mol } H_2SO_4\end{aligned}$$

Acids react with metal hydroxides to form water and a salt. Thus, the balanced equation for the neutralization reaction is:

$$H_2SO_4\,(aq) + 2\,\text{NaOH}\,(aq) \longrightarrow 2\,H_2O\,(l) + Na_2SO_4\,(aq)$$

According to the balanced equation, $1\ \text{mol } H_2SO_4 \simeq 2\ \text{mol NaOH}$. Therefore,

$$\begin{aligned}\text{Moles NaOH} &= (2.28 \times 10^{-2}\ \cancel{\text{mol } H_2SO_4})\left(\frac{2\ \text{mol NaOH}}{1\ \cancel{\text{mol } H_2SO_4}}\right)\\ &= 4.56 \times 10^{-2}\ \text{mol NaOH}\end{aligned}$$

Knowing the number of moles of NaOH in 20.0 mL of solution allows us to calculate the molarity of this solution:

$$\begin{aligned}\text{Molarity NaOH} &= \frac{\text{mol NaOH}}{\text{L soln}}\\ &= \left(\frac{4.56 \times 10^{-2}\ \text{mol NaOH}}{20.0\ \cancel{\text{mL soln}}}\right)\left(\frac{1000\ \cancel{\text{mL soln}}}{1\ \text{L soln}}\right)\\ &= 2.28\ \frac{\text{mol NaOH}}{\text{L soln}} = 2.28\ M\end{aligned}$$

Appendix C: A Summary of Problem-Solving Aspects for Each Question

<u>Question 1</u>

Problem Conceptualization

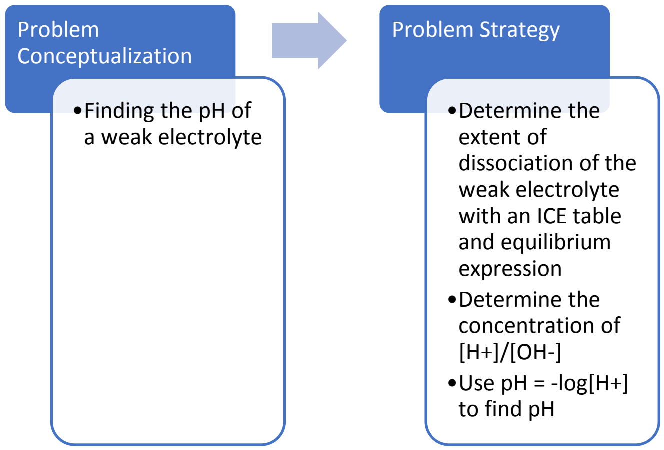
- Finding the pH of a strong electrolyte

Problem Strategy

- Determine the concentration of [H+]/[OH-]
- Use pH = -log[H+] to find pH

	Prior Knowledge	Essential Skills Demonstrated	Bottom-Up Processes and Heuristics Used
Students in Both Courses	- pH = -log[H+] - pOH = -log[OH-] [Base Version] - pH + pOH = 14 [Base Version]	- Identifying a strong electrolyte - Understanding dissociation of strong electrolytes - Calculating pH - Converting between pOH and pH [Base Version]	- Failing to account for 1:2 dissociation of a strong electrolyte [Base Version]
General Chemistry Students	--	--	--
Analytical Chemistry Students	--	--	- ICE tables - Henderson-Hasselbalch Equation

Question 2



	Prior Knowledge	Essential Skills Demonstrated	Bottom-Up Processes and Heuristics Used
Students in Both Courses	- pH = -log[H+] - pOH = -log[OH-] [Base Version] - pH + pOH = 14 [Base Version]	- Identifying a salt solution - Utilizing an ICE table - Writing equilibrium expressions - Calculating pH - Converting between pOH and pH [Base Version]	- ICE table - Henderson-Hasselbalch equation
General Chemistry Students	--	--	--
Analytical Chemistry Students	- Writing equilibrium expressions - Using K_a and K_b	--	--

Question 3

Problem Conceptualization

- Finding the pH of a salt solution

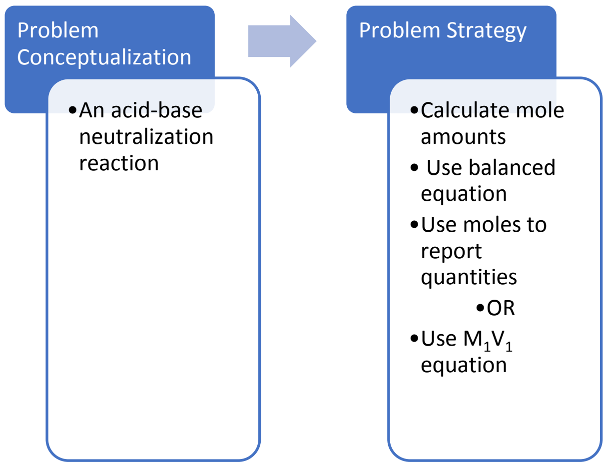
→

Problem Strategy

- Recognize the acid-base components of a salt solution
- Determine the extent of dissociation of the weak electrolyte with an ICE table and equilibrium expression
- Determine the concentration of [H+]/[OH-]
- Use pH = -log[H+] to find pH

	Prior Knowledge	Essential Skills Demonstrated	Bottom-Up Processes and Heuristics Used
Students in Both Courses	- pH = -log[H+] - pOH = -log[OH-] [Base Version] - pH + pOH = 14 [Base Version]	- Identifying a salt solution - Utilizing an ICE table - Writing equilibrium expressions for the conjugate acid or base present - Calculating pH - Converting between pOH and pH [Base Version]	- ICE table - Henderson-Hasselbalch equation
General Chemistry Students	--	--	--
Analytical Chemistry Students	- Writing equilibrium expressions - Using K_a and K_b	--	--

Question 4



	Prior Knowledge	Essential Skills Demonstrated	Bottom-Up Processes and Heuristics Used
Students in Both Courses	--	- Identifying strong electrolytes - Understanding dissociation of strong electrolytes - Understanding solution qualities such as concentration	- Failing to account for1:2 dissociation of a strong electrolyte - M_1V_1 equation
General Chemistry Students	- Dimensional analysis of an acid-base neutralization reaction	--	--
Analytical Chemistry Students	--	--	--

Question 5

Problem Conceptualization

- The region of a strong electrolyte-weak electrolyte titration where the strong electrolyte is in excess

Problem Strategy

- Identify the reaction between a strong and weak electrolyte
- Determine that the strong electrolyte is in excess
- Calculate the pH after accounting for the stoichiometry of the neutralization reaction and the increase in the solution volume

	Prior Knowledge	Essential Skills Demonstrated	Bottom-Up Processes and Heuristics Used
Students in Both Courses	- Identifying strong and weak electrolytes - Accounting for the stoichiometry of the neutralization reaction - pH = -log[H+] - pOH = -log[OH-] [Base Version] - pH + pOH = 14 [Base Version]	- Identifying strong and weak electrolytes - Determining titration region - Accounting for the stoichiometry of the neutralization reaction - Calculating pH - Converting between pOH and pH [Base Version]	- Henderson-Hasselbalch equation
General Chemistry Students	--	--	- BCA table

Analytical Chemistry Students	- Accounting for the dissociation of a weak electrolyte	--	- ICE table - Equilibrium expressions